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MECHANISM OF CRYSTAL GROWTH, ETCHING AND TWIN FORMATION OF HEMATITE*

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Abstract

The surface structures of hematite crystals from nine localities are observed with an ordinary reflecting and a phase contrast microscope, and the step heights of growth layers as well as the other surface features are measured precisely with multiple-beam interferometric method and the method of fringes of equal chromatic order. On the basis of these observations and measurements, mechanism of crystal growth, natural etching, twin formation and movement of screw dislocations after the cessation of growth and the possibility of polytypism are discussed in this paper. Physical and chemical conditions under which hematite crystals have grown are also discussed on the basis of characteristics of growth and etch patterns.

Introduction

If the surface of a crystal face is examined under a reflecting microscope, the surface structure which looks like contour lines of a topographic map is observed. If proper methods of observation are used, these contour lines can be observed on every predominant crystal face, even if the face is very flat like a mirror. The contour lines are sometimes polygonal according to the symmetry of the face, and in other cases circular or irregular. They are without doubt the edges of two-dimensional layers parallel to the crystal face, and are considered to show the final stage of crystal growth or etching. Therefore, it is possible to know the mechanism of crystal growth and etching through observations of the surface structures of crystal

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faces. Since the different crystallization conditions will produce different surface structures, it is also possible to presume physical or chemical conditions of crystal growth by studying the surface structures of crystal faces. Furthermore, since the existence of imperfections inside a crystal, such as dislocations, impurities, etc., will affect the forms of growth patterns, surface topographic studies of crystal faces will offer a good chance of direct observation of these internal imperfections of crystals. In fact, it is through the observations of the surface structures of crystal faces that the layer growth theory proposed by Stranski[15], Kossel[13], etc., the spiral growth theory by Frank[7] and the hypothesis concerning the existence and behavior of dislocations in crystals have been established.

Recent development in methods of observation or measurement such as phase contrast microscopy or multiple-beam interferometry have made possible to extend the observable and measurable scope to the order of one unit cell of a crystal or less than that. Therefore, if we use the highest technique of these methods, it is possible to discuss the mechanism of crystal growth or etching in terms of one unit cell or one minimum constituent in the unit cell.

It is the main purpose of this paper to describe what kinds of informations can be obtained through the observations of the surface structures of crystal faces, mainly by introducing the result of studies on hematite crystals by the present writer.

Methods of observation and measurement of the thicknesses of layers

Crystal faces are observed under an ordinary microscope, after cleaning the surface with hydrogen peroxide, detergent solution and water. Silvering the surface in a vacuum evaporation plant usually improves reflectivity of the face, and makes possible to observe layers having very small step heights, but the crystal faces of hematite have reflectivities high enough to observe ultra thin layers without silvering.

Although thick layers can be observed easily under an ordinary reflecting microscope, it is almost impossible to observe layers thinner than a few hundreds of angstrom, unless the phase contrast microscope is used. If the specimen having high reflectivity and smooth surface is observed under a powerful phase contrast microscope, and the observer is trained enough in observing thin layers with the phase contrast microscope, it is possible to see the layers having ten angstroms thickness directly under the microscope. It is also possible to take photomicrograph of the layers having a few angstroms step height, if very high contrast film is used. Since the height of one unit cell of hematite is 13.73 Å. in the direction of c-axis, it can be said that the ability of the phase contrast microscope used in this study is more than adequate to observe every sort of surface structures on hematite crystals. Another advantage of phase contrast microscopy is that it is possible to know which side of a step is higher, from the position of white diffraction band appearing along the step. In the case of positive phase contrast, white band always appears on the higher side of a step, and vice versa in the case of negative phase contrast.

Multiple-beam interferometry which has been developed by Tolansky[24) 25)] is the most powerful and accurate method in measuring the thicknesses of thin layers. The surface of both the crystal face and the optical flat are silvered in a vacuum evaporation plant to a proper thickness, respectively. The best result can be obtained when the optical flat is silvered to a thickness of about 80% reflectivity and a thickness nearly 100% reflectivity for the crystal surface. It is proved that silvering does not modify the surface topography[26)], if the thickness of silvering is less than 6,000 Å. Two silvered surfaces are matched, and let parallel monochromatic light (green mercury light λ=5,461 Å. is usually used) pass through the optical flat, then multiple reflection occurs between these two silvered surfaces. As a result, sharp, high precision multiple-beam Fizeau fringes are produced. Since the fringes thus obtained are much sharper than

those obtained by a usual two-beam interferometry, very accurate measurement of the step heights can be done with this method. In normally good conditions, it is not difficult to measure step heights down to 15 Å. In the case of thinner layers than this value, average step heights can be obtained by indirect methods. For instance when the spacing between the successive layers of a very shallow spiral is close regular and narrow, it is easy to calculate the average step height of a single layer by dividing the easily measured total height of the spiral by the number of layers.

If a fringe obtained by the similar method but using white light instead of monochromatic light is analysed by a spectroscope, several fringes of similar form are obtained. These fringes are called FECO (fringes of equal chromatic order) and the method has also been developed by Tolansky. It is possible from the fringes of this method, (1) to measure step height very accurately, (2) to determine definitely whether a pattern is an elevation or depression. Details of these methods can be refered to the original books by Tolansky[24) 25)].

Growth patterns and the mechanism of crystal growth[21)]

A large number of hematite crystals from the following nine localities have been observed.

Japan: Ayumikotan, Sasazawa, Gihofuji, Saganoshima.

Abroad: The Azores Islands, Vesuvius, Stromboli, Ascension Island, British West Indies.

All these crystals occur in volcanic lavas and aggromerates, and are considered to be formed when iron chloride gas, which migrates from magma reservoir as a post volcanic action, meets oxidation condition such as underground water. Crystals have thin tabular habits parallel to the basal plane, on which various growth patterns are observed.

(A) *Observations under low magnification*

Patterns which look like contour lines of a topographic map are

observed on the basal planes of all hematite crystals observed in this study. They are mainly circular or irregular and have one or a few centres (the highest parts on the surface) on one face. These centres are peaks of mountains on a topographic map. An example of general surface patterns is shown in Fig. 1. Crystals from Gihofuji and Ascension Island (I) show triangular patterns instead of circular or irregular ones, and also have one or a few centres. When there are small hematite crystals inclined to the basal plane or impurity materials on the surface, a pattern which is similar to the back current formed behind a rock in a stream is observed around them, an example being shown in Fig. 2. These facts clearly show that the patterns observed on the basal plane are formed by growth, and that the growth of hematite crystals mainly takes place by two-dimensional spreading and piling up of layers, which originate from some centres, parallel to the basal plane.

It is often observed, (1) that the surface is broken up at a growth centre forming many small portion which are inclined to the original basal plane with a small angle (Fig. 3), (2) that thick spiral growth layers originate from the end of slightly inclined portions on the surface (Fig. 4), and (3) that small misorientated hematite crystals are situated at the centre of growth. These observations suggest that the thick growth layers mainly originate from the portions which are actually broken up during growth due to external or internal stresses or from the portions which receive impact of other crystals.

Entirely different surface patterns from those of the basal plane described above are observed on the faces other than the basal plane, such as $r\{10\bar{1}1\}$, $m\{10\bar{1}0\}$, $a\{1120\}$ and $\{hk\bar{i}l\}$. Striations parallel to the edges between the face and the basal plane are the only feature which can be observed on any kinds of $\{hk\bar{i}l\}$ faces, and on the *r*, *m* and *a* faces when they are small. This clearly shows that these faces are formed by piling of the edges of the growth layers on the basal plane. When *r*, *m* and *a* faces develop, irregular growth layers parallel to these faces develop on the surface and mainly start from

the edges with the basal plane. The forms of these growth layers are strongly effected by the direction parallel to the basal plane as shown in Fig. 5. This fact suggests that the growth of hematite crystals mainly takes place on the basal plane, and the faces other than the basal plane are formed by piling up of the layers on the basal plane at the early stage, and only at the later stage growth layers can develop on themselves.

(B) *Observations under a phase contrast microscope*

If the surfaces of the growth centres described above are observed under the phase contrast microscope, one of the following patterns is observed.

1. Many thin spiral-like growth layers originate from an aggregation or a line (curved or straight) of screw dislocations. Each spiral-like growth layers does not form an independent spiral pattern even at its centre. Fig. 6 shows an example of these patterns. It is often observed that a part of the surface near the line or aggregation of screw dislocations is inclined or folded to the original basal plane. This shows that the aggregation or the line is formed by the deformation of the surface due to a kind of stresses applied to the crystal.
2. Many independent spirals occur in a small area on the surface of a growth centre (Fig. 7). Thin growth layers originating from these spirals cover the surface of the growth centre, and bunch together to form thick growth layers. This is considered to show that screw dislocations already existed in the crystal move and concentrate into a small area, probably due to stresses applied to the crystal while it is growing.
3. Nearly the whole surface of a basal plane is covered with very thin spiral growth layers originating from one or a few screw dislocation points. These spirals always have typical form which is theoretically expected.

Among these three patterns, 1 and 2 are most commonly observed while 3, the typical spiral, is observed only on a small number of

crystals from a few special localities. Both the patterns of 1 and 2 show that the main growth centres from which growth layers mainly originate are a kind of deformed portions of the surface. These deformed portions are formed by actual break up of the surface, or concentration of many screw dislocations into a small area through the movement of dislocations during growth, both probably due to external or internal stresses applied to the crystal. Since steps, kinks or screw dislocations are concentrated in such deformed portions, growth will preferentially and predominantly originate, forming growth centres. These observations again show that stresses applied to the growing crystals are the main cause of promoting crystal growth. The pattern 3, typical spiral, is considered to be formed without any disturbance at the latest stage of crystallization under very low supersaturation condition, since the spacing between successive spiral layers is very wide compared with that of the other spirals.

Although spiral patterns are observed on almost all crystals studied, no spiral has been observed on the crystals from Ascension Island (I). The surfaces of these crystals consist of thick triangular growth layers. If the surfaces of these thick triangular layers are observed under the phase contrast microscope, it is found that they consist of many very thin triangular growth layers and that there is no spiral at all on the surfaces, as is shown in Fig. 8. It is also observed on one crystal from Saganoshima that the surface consists of two different patterns; one is a typical triangular spiral having 7 Å. step height, the other is triangular growth islands and tongue-like terraces having step heights of about 40 Å., on which no spiral can be seen. From the relation between these two patterns, it is found that the triangular growth islands and tongue-like terraces are formed at first by two-dimensional nucleation without a help of screw dislocations, and then the triangular spiral is formed at the later stage of crystallization[19]. Since very high supersaturation such as more than 25% is necessary to form a growth island on the surface of a crystal by two-dimensional nucleation[15], it is believed that

these crystals and the triangular islands grew under a very high supersaturation, probably at the earliest stage of crystallization.

Various kinds of spiral patterns are also observed on the surface of thick growth layers. In these cases too, the most common features are complex spirals originating from a line or a group of screw dislocations which are genetically related to the deformation of the surface due to stresses applied to the growing crystals. However, it is also observed on some crystals that the surface of a thick growth layer consists of many independent spirals as shown in Fig. 9. These spirals are clearly formed at the latest stage of crystallization on the surface of thick growth layers which were already formed.

Although in some cases a growth layer may appear from the beginning as a thick layer, in other cases it is evidently formed by bunching of thinner layers. The advancing speed of a thin layer decreases as the layer spreads or when the layer meets impurities, etc.. Once the speed of the first layer decreases, the next thin growth layer will catch up the first one forming a thicker layer. Once a thick layer is formed, the thickness of the layer will increase rapidly, as the advancing speed of thicker layer is much slower than that of thinner layer under the same condition of growth. Thus thick growth layers such as having step heights of a few thousands of angstrom are formed by bunching of very thin growth layers having less than 10 Å. step height. Generally speaking, thin growth layers have smooth and regular fronts, while thick growth layers formed by bunching of thinner layers have irregular fronts. This relation can be seen on the growth patterns of many crystals, an example of which is shown in Fig. 10.

(C) *Mechanism of crystal growth of hematite*

From the observations described above, the mechanism and the process of crystal growth of hematite can be summarized as follows.

At the earliest stage of crystallization, when the rate of supersaturation is high, crystal growth seems to take place mainly through two-dimensional nucleation, from which growth layers spread and

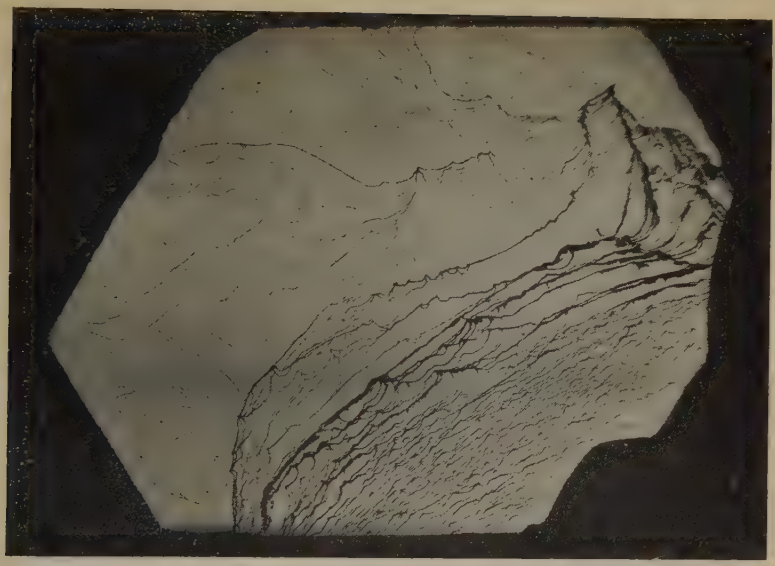

Fig. 1. General surface structure of the basal plane of hematite. Two growth centres are observed. Vesuvius. ×6.

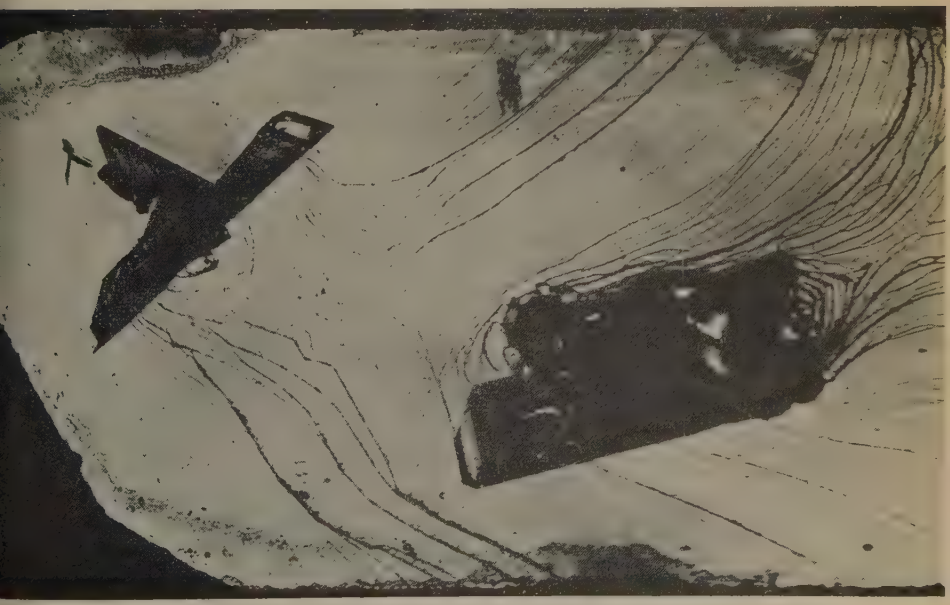

Fig. 2. Showing the growth pattern formed behind misorientated small hematite crystals on the basal plane. Saganoshima. ×20.

Fig. 3. Ordinary photomicrograph of a "broken up" portion. Black portions on the photograph are slightly inclined to the basal plane. Saganoshima. ×15.

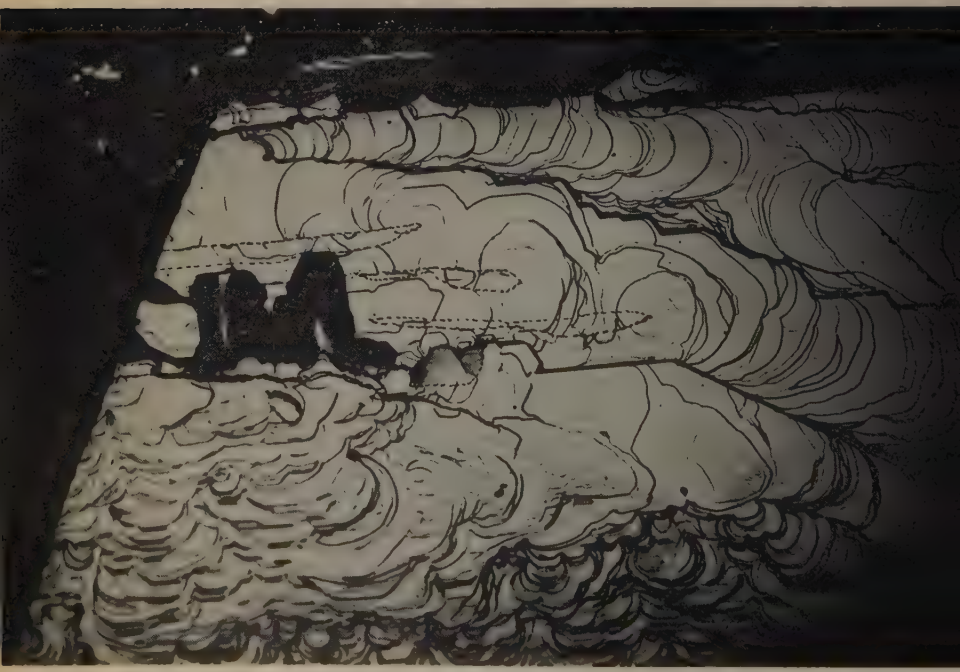

Fig. 4. Showing inclined portions from which thick spiral layers originate. Dotted lines show inclined portions. The Azores Islands. ×50.

Fig. 5. Growth layers on the surface of r (10$\bar{1}$1) face. Ayumikotan. ×6.

Fig. 6. Positive phase contrast photomicrograph of a growth centre. Ayumikotan. ×300.

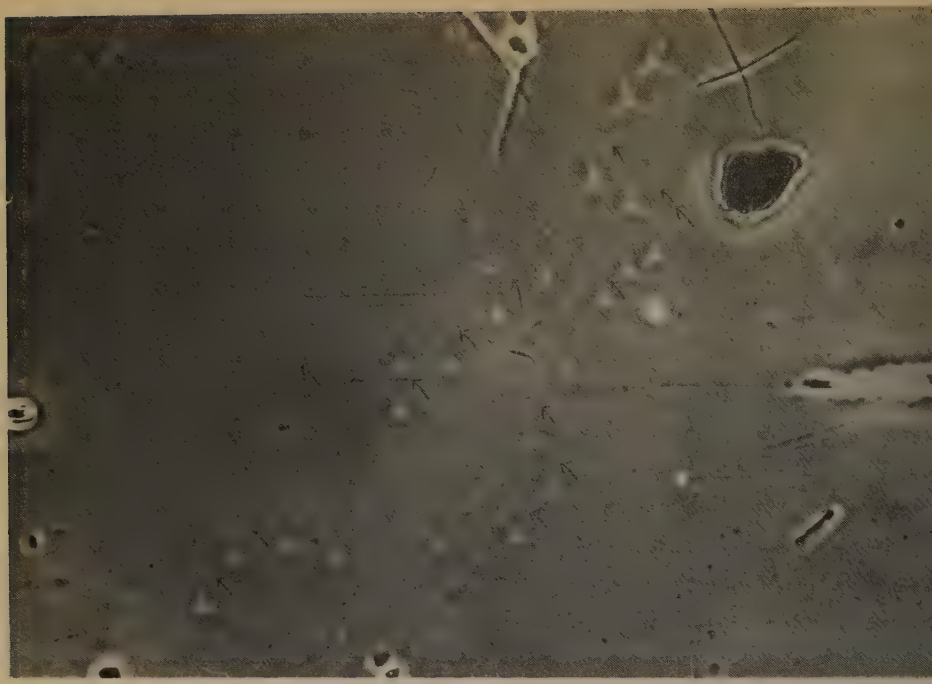

Fig. 7. Positive phase contrast photomicrograph of a growth centre of Type 2. Triangular cones seen in the photograph consist of narrow spaced triangular spirals having step height of 2.3 Å. Lines formed by the movement of dislocations after the cessation of growth are also clearly seen in the photograph. They are shown by arrows. Saganoshima. ×300.

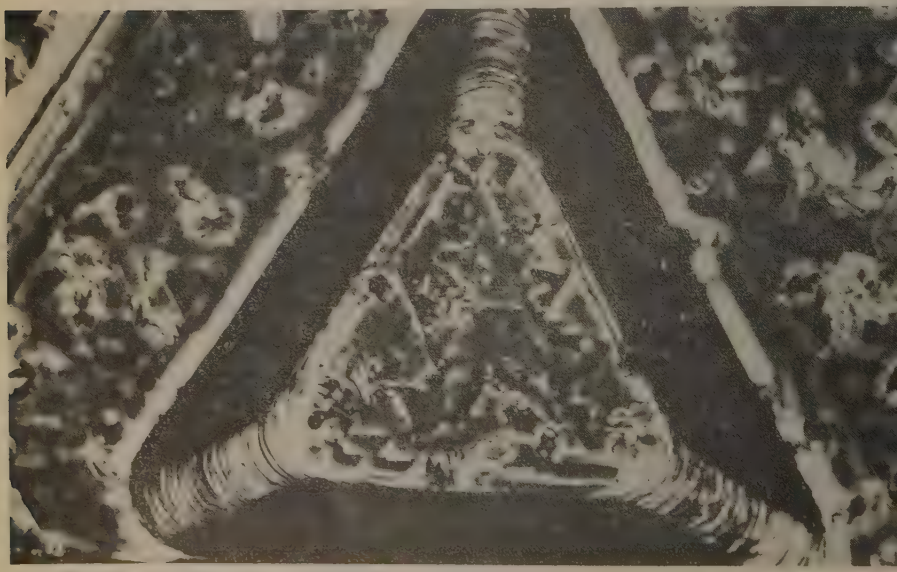

Fig. 8. Positive phase contrast photomicrograph of triangular growth layers. Ascension Island I. ×270.

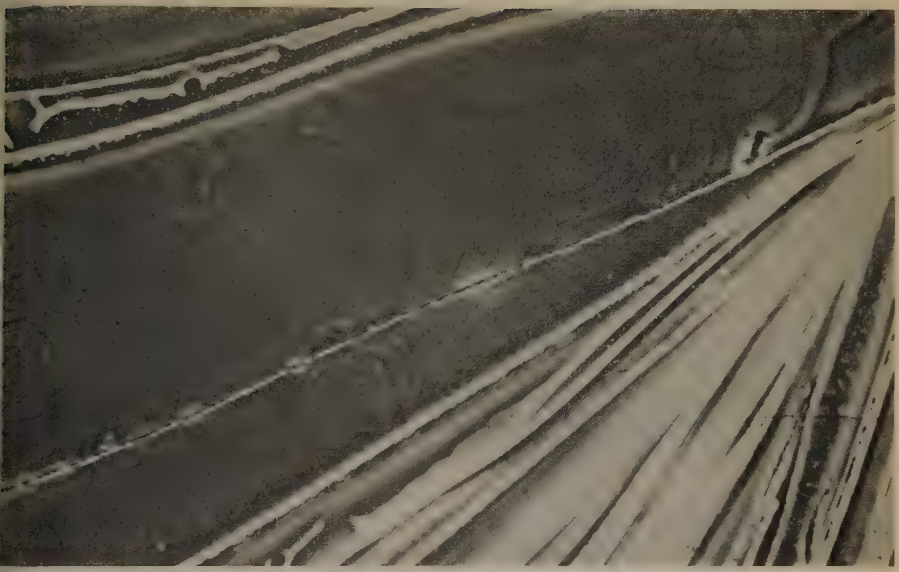

Fig. 9. Positive phase contrast photomicrograph showing many independent spirals on the surface of thick growth layers. The Azores Islands. ×300.

Fig. 10. Positive phase contrast photomicrograph showing bunching of thin growth layers. British West Indies. ×300.

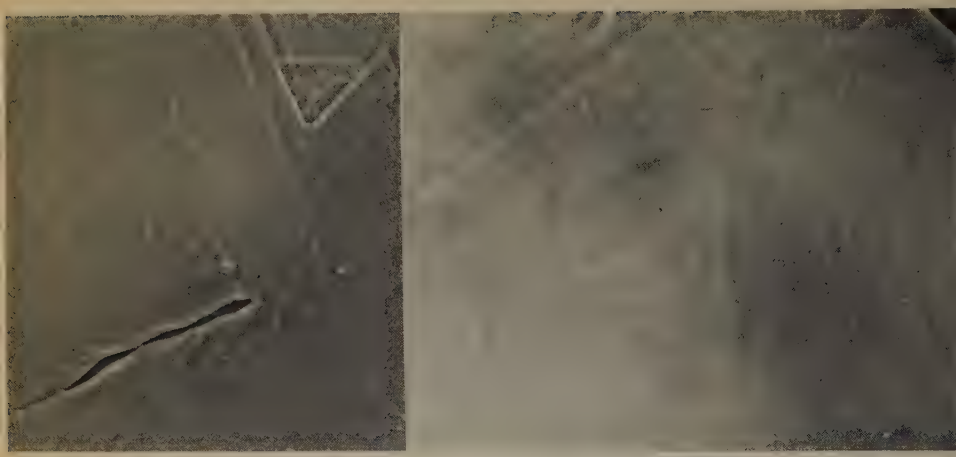

Fig. 11a, b. Positive phase contrast photographs showing 2.3 Å. spiral. Under low magnification, it appears as a triangular cone (Fig. 11a, ×150), but higher magnification reveals that the cone consists of a narrow spaced triangular spiral (Fig. 11b, ×2,100). Ayumikotan.

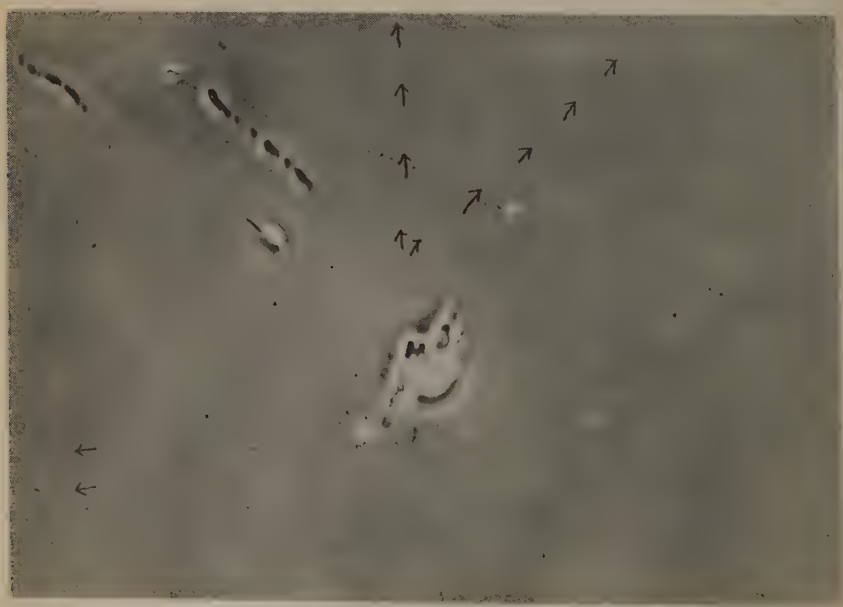

Fig. 12. Positive phase contrast photomicrograph of a 4.6 Å. spiral. Arrows show horn-like projections formed by the difference of advancing speed in different directions. Saganoshima. ×300.

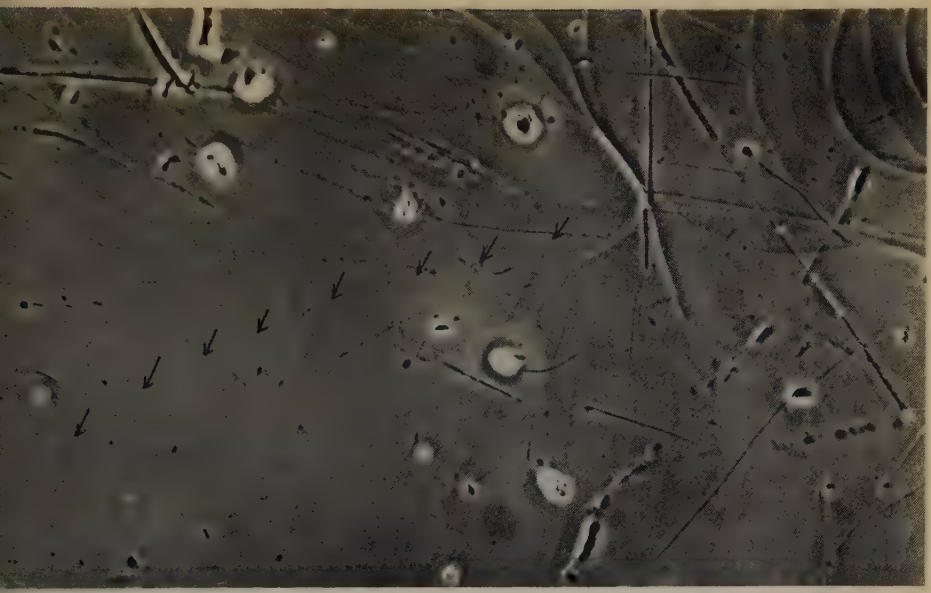

Fig. 13. Positive phase contrast photomicrograph showing an interlacing pattern formed on a 21 Å. spiral. Arrows show the positions where layers split into two. Saganoshima. ×350.

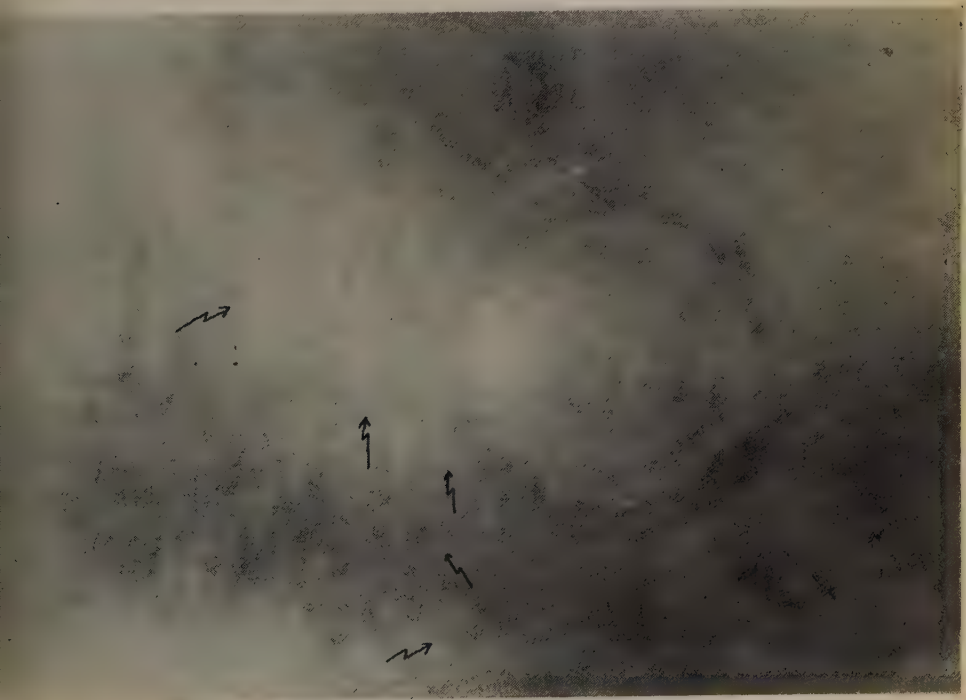

Fig. 16a. Positive phase contrast photomicrograph showing the movement of screw dislocations after the cessation of growth. Arrows show the lines formed by the movement of dislocations. Ascension Island II. ×300.

Fig. 16b. Positive phase contrast photomicrograph of the basal plane of a hematite crystal from Vesuvius. This complicated surface pattern is formed by movement of screw dislocations. ×300.

pile up. Screw dislocations will play no role at this stage. When a crystal thus formed reaches a certain size, a part of the surface of the crystal will be bent, folded or broken up, because of (1) internal stresses, (2) external stresses and (3) impact of other crystals. Due to this bending or folding, screw dislocations already existed in the crystal will move and concentrate into a small area (a kind of polygonization). In some cases the surface is actually broken up forming portions which are inclined to the original surface with a small angle. The boundaries between these portions and the original surface are a kind of twist boundaries which consist of crossed grid of screw dislocations. Therefore, growth will preferentially take place at these portions on the surface, and the growth layers will rapidly spring out from them, forming growth centres. Thin growth layers thus originated will bunch together forming thicker layers. Since the supersaturation rate is still high at this stage, growth layers will rapidly spread out. As a result, even if there are screw dislocations terminated on the other part of the surface, independent spiral patterns can not freely be formed from them, since the thick growth layers from the main growth centres overwhelm and possibly engulf the thin spiral growth layers originating from isolated screw dislocations. As supersaturation rate decreases, advancing speed of thick growth layers will slow down, and finally their spreading will stop. Then growth layers can freely originate from the screw dislocations already existed, forming typical spirals. Spirals observed on the surface of thick growth layers as well as the typical spirals which cover nearly the whole surface of a crystal face are formed at this stage.

Crystals from different localities show different growth patterns. For instance, crystals from Ascension Island (I) do not show spirals, while typical spiral patterns can be observed on crystals from The Azores Islands, Saganoshima and British West Indies. According to the calculation by Burton et al.[5], two-dimensional nucleation will not take place unless supersaturation rate is higher than 25%, in the

case of crystals produced by gas reactions. It can be qualitatively said from the equations concerning the relation between the spacing between successive layers of a spiral and supersaturation rate that the lower the supersaturation rate is, the wider the spacing. Therefore, it is possible to presume the supersaturation condition at the time of crystal growth at each locality from the characteristics of the growth patterns. As a result of observations on many crystals from nine localities, it can be said that the crystals from Ascension Island (I) have grown under the very high supersaturation; then those from Gihofuji, Ayumikotan, Stromboli, Vesuvius and Sasazawa come to the next; while those from Saganoshima and The Azores Islands have grown under very low supersaturation condition.

(D) *Unit of growth* (*step heights of spirals*)[17) 20)]

It was previously thought that crystal growth took place by the precipitation of particles consisting of many unit cells. As a result of precise measurement of the thickness of spiral layers by Amelinckx[2)], Verma[28)], etc., it was found that the thicknesses of spiral layers were one unit cell high or a small rational multiple of a unit cell. Therefore, it has recently been generally believed that the unit of growth is in the order of one unit cell. However, the unit cell of the crystal is defined mainly according to the geometrical characteristics of atom arrangement rather than to the physical or chemical nature of the crystal. It is not natural to think that crystal growth which is originally a physical or chemical phenomenon ought to be controlled by the geometrical nature of the crystal alone. Therefore, precise re-investigation of the thickness of spiral layers is most necessary in the study of crystal growth.

The writer has measured precisely the thickness of spiral layers on the basal plane of hematite crystals, using multiple-beam interferometry and FECO. In many cases, it is difficult to measure the step height of a spiral layer directly from the shift of fringes, as the step height is too small to secure a measurable shift on the fringe. However, since the spacings between successive layers of the

typical spiral are close regular in many cases and the step heights of spiral layers originating from one screw dislocation are always the same, it is possible to obtain an average step height of the spiral layers by dividing the total height of the spiral by the number of the layers. By measuring the step height of a thick layer formed by bunching of thinner layers and counting the number of these thinner layers, an average step height of the thinner layers can also be easily obtained. The indirect methods described here will give more accurate results than the direct measurement of the step height from the shift of fringes.

Since details of the result of measurements will be published elsewhere[20], only the final result is presented here. As a result of precise measurements of the step heights of spiral layers on hematite, it is confirmed that there are spirals having step heights of 2.3 Å., 4.6 Å., 7 Å., 10 Å. and 21 Å.

Among those, the 2.3 Å. spirals always show regular triangular form (Fig. 11); the 4.6 Å. spirals show triangular form having three corners truncated, and a special pattern formed by the difference of advancing speed in different directions can be seen at six corners (Fig. 12); in the case of the 7 Å. spirals, two spirals always originate either from two screw dislocation points of opposite sense situated close together or from one screw dislocation point (in this case two spirals have the same sign); layers of the 21 Å. spirals always split into two on the way of spreading, forming an interlacing pattern (Fig. 13).

Now, the crystal structure of hematite can be interpreted as a layer structure, as schematically shown in Fig. 14. The height of one unit cell is 13.72 Å. in the direction of c-axis. One unit cell contains six layers of Fe-O-Fe, and triangles consisting of three oxygen atoms have opposite direction in successive layers. Therefore, as can be seen from the result of measurements, the smallest height of growth layers, in other words the unit of growth of hematite, is not equal to the height of a unit cell, but the height of the single con-

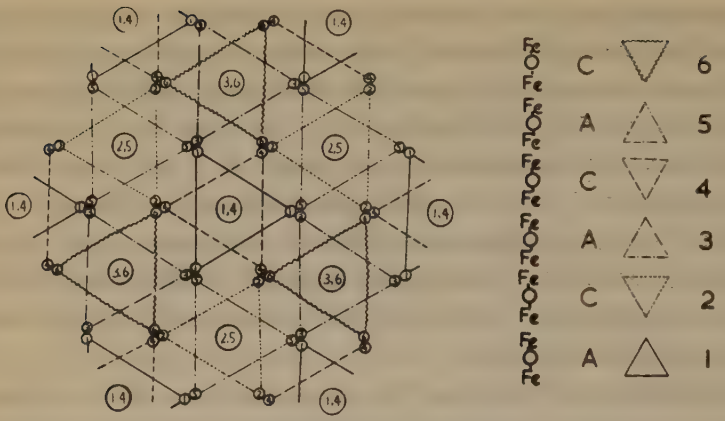

Fig. 14. Schematic drawing of the unit cell of hematite.
Left: plane, Right: profile.

stituent layer in the crystal. The thickness of the other spiral layers is a rational multiple of this unit of growth. Therefore, the widely accepted belief on the unit height of spirals is here contradicted.

Morphological characteristics of each spiral also support the results of measurements. Since the 2.3 Å. spirals consist of a single layer in the unit cell, they show regular triangular forms. As the 4.6 Å. spirals consist of two layers having opposite triangles, they always show truncated triangles. Since 7 Å. is a half of a unit cell and one unit cell can split into two, two screw dislocations always exist close together. Because 21 Å. is one and a half unit cell height, the growth layers originating from such a screw dislocation will split into two layers forming an interlacing pattern.

That the minimum height of growth layers is not one unit cell height but equal to the height of the single constituent layer in the crystal will possibly hold good with other crystals which have layer structure, such as mica group or silicon carbide. In fact Amelinckx reported a spiral having a half of unit cell height on silicon carbide[1] and n-alcohol[3]. The writer also measured step height of 5 Å., which is a half of a unit cell of 4H type of silicon carbide.

However, in this case, the smallest step height of growth layers, so far as reported, is not the height of single constituent layer in the unit cell but that of two layers.

Movement of dislocations after the cessation of growth[16) 19)]

It was theoretically predicted and experimentally established that dislocations can move easily by stresses or forces applied to the crystal.

Movement of screw dislocations during growth is already discussed earlier in this paper. In this section, an account will be given of several good examples showing the movement of screw dislocations after the cessation of growth. It is also briefly discussed on the relation between the history of stress which crystals received after the end of growth and the frequency and the amount of movement of dislocations.

It is often observed on some crystals that a straight line starts from a screw dislocation point and runs across the spiral layers, an example being shown in Fig. 16a. The direction of the line is always crystallographically rational, that is parallel to one of the three horizontal crystal axes. When it meets the edges of spiral layers, it does not give any disturbance or shift of the edges. This shows that the line is formed after the formation of the spiral pattern. There is always a level difference on both sides of the line. Looking from the centre of a spiral, left side of the line is always the higher side in the case of the line starting from a right-handed spiral, and vice versa. As can be seen from the process of the formation of a spiral, the right-handed spiral is formed from the screw dislocation which has higher side on the right, looking from the dislocation point, and vice versa (Fig. 15a). Therefore, the observed line is clearly not the original dislocation line. If an original screw dislocation moves towards the front after the formation of a spiral pattern, a line which has higher side on the right should appear in

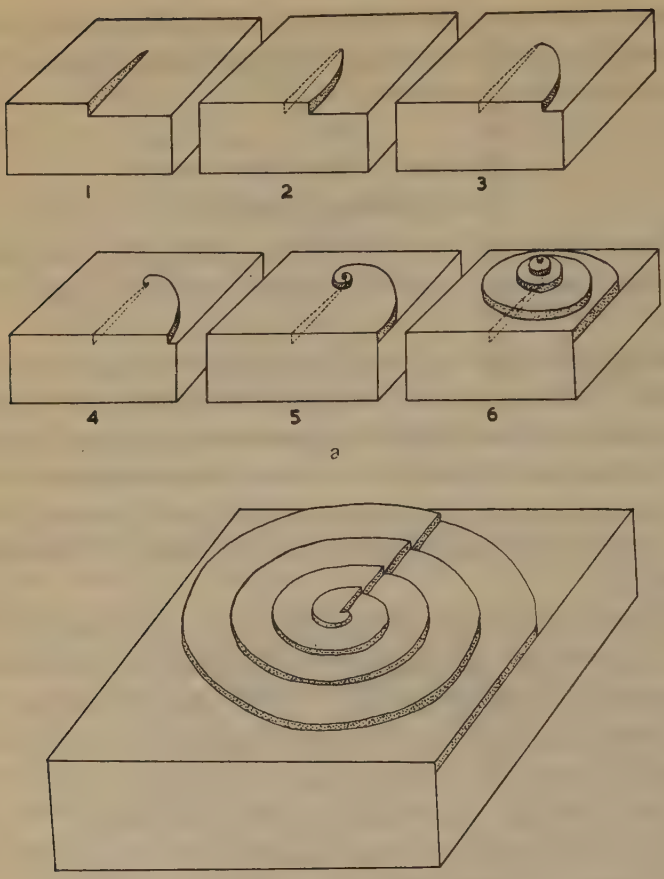

Fig. 15a. Schematic figures showing the process of formation of a spiral pattern at a screw dislocation.
b. Showing the movement of screw dislocation after the cessation of growth.

the case of the left-handed spirals, and vice versa as can be seen in Fig. 15b. Therefore, it can be safely concluded that the observed line is the line formed by the movement of a screw dislocation after the cessation of growth.

Fig. 16b is a phase contrast photomicrograph of a part of the

surface of the basal plane of a hematite crystal from Vesuvius. On this photograph, it is observed that a group of straight lines of three directions is superimposed on the ordinary circular or irregular growth patterns. Since growth fronts never cross each other, the straight lines superimposed on the growth pattern are clearly not the edges of growth layers. It is observed at less complicated portion of the same surface that the straight lines originate from the centres of spirals and have the same characteristics as that of the lines described above. Thus, it is concluded that these lines are formed by the movement of screw dislocations after the cessation of growth, and that since there were many screw dislocations terminated on the surface and the crystal suffered a strong stress, such a complicated surface structure as in Fig. 16b has been formed.

The hematite crystals from Vesuvius show extremely high frequency and long distance of the movement of screw dislocations, while those from Gihofuji, Saganoshima, Ayumikotan, etc. do show either no movement or only a small movement. In the case of Vesuvius crystals, all crystals observed show remarkable movement, while in the case of crystals from the other localities the movement lines are observed on some crystals but not on other crystals, even if there are spirals on the surface. As is well known, Vesuvius is a very active volcano, while Saganoshima, etc. are rather quiet ones. Therefore, the frequency and the distance of movement of dislocations is considered to show the stress history of the crystal. It is explained that the crystals which suffered strong stresses due to volcanic activities, such as those from Vesuvius, will show remarkable movement of screw dislocation.

Possibility of polytypism in hematite[17]

If a crystal is of polytype, spirals observed on the crystal will show a special pattern which is called an interlacing pattern. Since the height of a unit cell of a polytype crystal is one and a fraction of that of the original cell, the spiral layers of the polytype will

split into two. As the two splitted layers have different advancing rate in the same direction, an interlacing pattern is formed, its process being schematically shown in Fig. 17. Therefore, from pattern of spirals, it is possible to know whether the crystal is of polytype. The relation between the spiral pattern and polytypism is remarkably demonstrated on silicon carbide, cadmium iodide and mica, by Verma[27) 28)], Amelinckx[2) 4) 6)], etc.

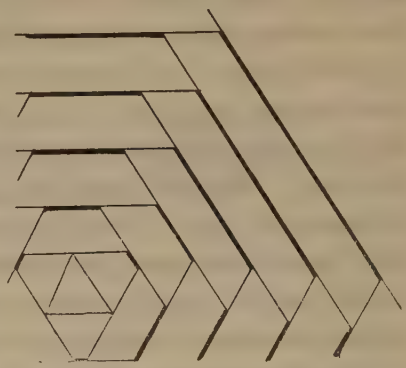

Fig. 17. Schematic figure showing the formation of an interlacing pattern.

Frank discussed theoretically the origin of polytypism, and concluded that different polytypes are produced by different Burgers' vector of screw dislocations[8)]. If a screw dislocation having Burgers' vector $\mathfrak{A}$ which is a fractional multiple of the original unit cell height terminates on the growing surface, the spiral originating from this dislocation will form a polytype, the unit cell of which is $\mathfrak{A}$. Mitchell supported this theory as a result of detailed structural consideration of silicon carbide and cadmium iodide[14)].

There has been no report on the existence of polytypism in hematite. The writer observed some evidences suggesting the possibility of polytypism in hematite on the surface structures of the basal plane.

The first example is the spiral having step height of 21Å. This spiral show typical interlacing pattern in one direction, and the Burgers' vector of the spiral is one and a half unit cell of hematite (Fig. 13). Therefore, this must be a polytype having the unit cell of 21Å. However, X-ray investigation on this crystal did not give a proof of polytype. The second example is observed on a crystal from Ayumikotan[17)]. Triangular cones which consist of many layers

are observed on the surface (Fig. 18a). Some of the triangular cones have very steep centres, which suggest that rapid growth took place at the latest stage. Observation under a high magnification with phase contrast reveals that the orientation of each triangular layer is opposite in successive layers or in every two or three layers. The observed combination can be expressed in the form of (AB), (ABAB′), (ABBB), etc.. An example of these patterns is shown in Fig. 18b. This surface pattern is a kind of interlacing. Therefore, X-ray investigations were carried out expecting the proof of polytypes on these portions, but in vain.

In the two cases above mentioned, the growth patterns suggest the existence of polytypes, but X-ray investigation has failed in verifying it. The X-ray method may have been inappropriate, because polytypic part may occupy only the topmost surface of the crystal, as the interlacing spirals are formed at the latest stage. It is desirable to verify the existence of polytypism in hematite by X-ray or electron diffraction methods in the near future.

Etching patterns and the mechanism of natural etching[22]

Many studies have been made on the etching patterns of natural minerals, such as by Ichikawa[11] and Horness[10]. They are mainly concerned with the morphology and the symmetry of the so-called etched figures or etched pits, and no special attention has been paid to the mechanism or process of etching. As a result, it is widely believed that etching mainly takes place in three-dimensional way. Etching has been one of the most important technique in the field of metallurgy, especially since the birth of dislocation theory. In this field too, however, etching is considered to progress in three-dimensional way at the dislocation points. There is only one theoretical paper by Frank[9] in which the mechanism of etching is discussed in terms of two-dimensional way.

The writer noticed that the surface structures of the crystals

from the Azores Islands are the patterns formed by natural etching, though they look like growth patterns in appearance. As a result of detailed observations of them by the phase contrast microscope, a few unexpected new informations concerning the mechanism of natural etching have been obtained, which are briefly described in this section.

(A) *Observations under low magnification*

The surface structures of the basal plane of hematite crystals from the Azores Islands differ from the growth patterns of the crystals from the other localities in the following points.

1. On many crystals, a large number of circular centres are found on the surface as shown in Fig. 19. They are all depressions. Such a large number of depression circles can never be formed by growth.
2. Contour lines, namely the edges of the layers parallel to the basal plane, show remarkable concave form looking from the higher side. It is theoretically impossible to form concave fronts by growth, as schematically shown in Fig. 20. Only in the case that etching takes place two-dimensionally, concave fronts can be formed, as illustrated in Fig. 20.

As the result of these considerations, it is concluded that the surface structures observed on the crystals from the Azores Islands are formed by two-dimensional etching. The direction of advance of etch fronts is, however, opposite to that of growth. In fact, the patterns similar to the back current formed behind a rock in a stream are formed by etching where there are impurities or

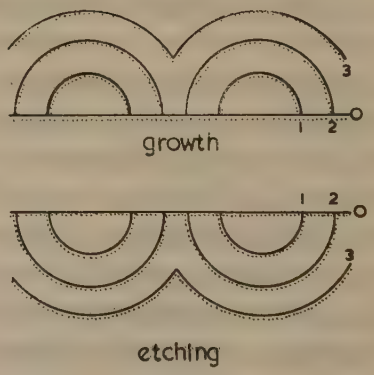

Fig. 20. Schematic figure of growth and etching fronts. Dots show higher side.

mis-orientated hematite crystals on the surface. Contrary to the case of similar patterns formed by growth, impurities, etc., play a role of obstacle against etching, forming unetched area behind them.

(B) *Observations by the phase contrast microscope*

The following facts are observed as a result of detailed examinations of the surface structures of hematite crystals from the Azores Islands, by means of phase contrast microscopy, multiple-beam interferometry and FECO.

1. Very small etched pits are uniformly distributed on the surface of many crystals. These pits are combined with each other forming irregular or triangular depressions, as etching progresses. Thus formed depressions are always flat bottomed, the surface of which is more fresh and smooth than the original surface (Fig. 21). The depth of the depressions is always from 40 to 60Å., namely twice or thrice as deep as the unit cell, and never exceeds it.
2. When there are thin spiral layers or thin growth layers, their edges consist of two lines; the outer line is smooth and the inner line is rugged. Between these two lines there lies one level deeper than the original part of the surface and with flat and fresh bottom. The depth of this ditch is also from 40 to 60Å. An example is shown in Fig. 22. These facts suggest that etching preferentially starts at the fronts of growth layers and develop two-dimensionally after the etched pit has attained to two or three unit cells depth. The profile of such a etched spiral is schematically shown in Fig. 23.

Fig. 23. Schematic profile of the etched spiral. Dotted line shows the original surface of the spiral, while dots show the present profile.

3. There is no evidence of overwhelmingly predominance of etching at the screw dislocation points of growth spirals, but etching at

the dislocation points is as strong as at the edges of the spiral layers.

4. Irregular depression spirals are usually observed at the bottom of circular depressions. One of the simplest depression spirals is shown in Fig. 24. The center of this spiral is the deepest point contrary to the usual growth spiral the centre of which has the highest elevation. The depression spirals usually have irregular or complicated form, and sometimes have saw-tooth edges. It is also often observed that such depression spirals originate from a line or a group of screw dislocations and form very complicated patterns.

Although crystals from localities other than the Azores Islands usually show typical growth patterns, the patterns formed by etching can be observed on some of them. The degree of etching is generally much weaker than that of the crystals from the Azores Islands but the patterns have similar nature. For instance, weak etching is observed along the edges of growth spirals on the crystals from Stromboli, and the concave fronts can be seen on some crystals from Ayumikotan. On the other hand, no evidence of natural etching has been found on the crystals from Gihofuji and Ascension Island.

(C) *Mechanism of natural etching*

Previous observations on etching are mainly concerned with morphology or symmetry of etched pits which are the parts where etching preferentially starts and progresses, while the observations by the present writer on hematite crystals cover the various stage of etching. Therefore, principal mechanism of etching becomes clear for the first time by the present observations.

Among the observed facts described in the section B, those of 2, 3 and 4 can be easily understood. If there are steps or the edges of screw dislocations exposed on the surface, they are the places which are most easily attacked by etching agent, as in the case of growth. If the surface is perfect and contains no imperfection such as steps, etching will not take place at all. Therefore, etching will

preferentially start at those imperfections. If etching starts at the edge of a growth layer, it will progress two-dimensionally, while if a screw dislocation is terminated on the surface (not a spiral pattern), etching front will rotate around the dislocation point forming a depression spiral. The process of the latter is the same as that of growth spiral, but opposite in its direction as schematically shown in Fig. 25.

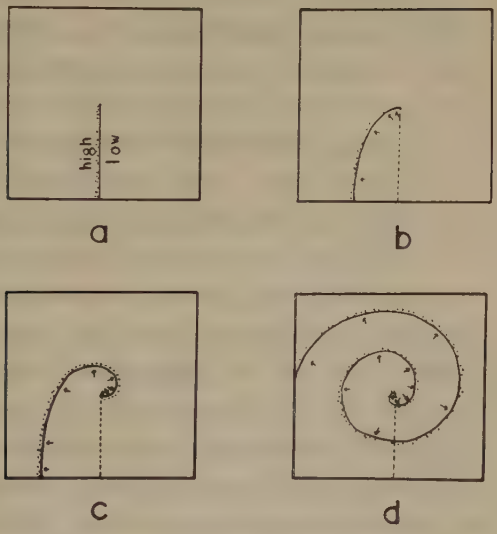

Fig. 25. Showing the process of formation of a depression spiral by etching. Dots show higher side, and arrows show the direction of advance of etching.

Special attention must be paid to the facts described in 1 and 2. These are; (a) fine pits formed by etching are distributed uniformly on the surface, (b) the pits and triangular depressions which are the progressed pits or formed by combination of many pits have flat bottoms, (c) the depths of these pits or flat-bottomed depressions are of the order of two or three unit cells depth, and (d) the surface newly exposed by etching is more fresh and smooth than the original surface.

These phenomena can not be interpreted with the knowledge on etching mechanism commonly believed. The writer's interpretation is as follows. When a crystal is growing, the topmost surface of the crystal is always unsaturated. The term "unsaturated" means that bonding is not completed and the surface contains many vacancies or lattice imperfections. As growth proceeds and new growth layers are formed on the original surface, the vacancies and imperfections in the original surface, which is now a part inside the crystal, will be filled up and become saturated. Therefore, when crystal growth ends, inside of the crystal will be saturated, while the topmost surface will remain unsaturated and contains lots of vacancies and imperfections. Etching will preferentially start from these imperfections on the surface. Etch pits distributed uniformly on the surface are those preferentially formed at these vacancies and imperfections. Etch pits thus started will deepen themselves to some extent, but when they have reached the saturated zone, they can no more deepen, because there are very few imperfections. As there are many imperfections in the unsaturated zone, it is easier for etching to progress sideways than to deepen three-dimensionally. Therefore, etching mainly progresses in two-dimensional way after the pits have reached the saturated zone, and flat-bottomed depressions, rather than deep etched pits, are formed. The surface thus exposed will be fresh and smooth, since it is the surface of the saturated zone. That the depths of flat-bottomed depressions and etched pits, etc. are in the order of two or three unit cells depth suggests the depth of the unsaturated zone.

All hematite crystal observed in this study is formed as a result of post volcanic action, when iron chloride gas meets oxidation condition such as underground water. Therefore, after forming hematite, Cl will combine with H forming HCl, which is a strong etching agent for hematite. If there is the more quantity of water, the more HCl will be formed, resulting in the more strong etching of hematite crystals. In fact, the Azores Islands are submarine volcanoes,

and it is most probable that the hematite crystals from this locality are formed under the sea, and hence they display much stronger etching effects than the crystals from the other localities. That the crystals from Ayumikotan, Saganoshima and Stromboli show etching effects to some degree, though weaker than in the case of the Azores Islands, may be attributed to their occurrence near the sea shore or in marine island. On the contrary, the crystals which occur in lavas of inland volcanoes, such as Vesuvius, Sasazawa and Gihofuji, do not show etched pattern at all. Thus, the degree of etching may be correlated to the crystallization environment.

Twins and the mechanism of twin formation

(A) *Contact twin*[18]

The contour lines observed on crystal faces are generally smooth and continuous, while on some crystals one or a few straight or curved lines cross the whole surface, and small but sharp shifts or kinks are formed where contour lines meet these lines. It is rather difficult to observe these lines directly under an ordinary reflecting microscope, but they can be seen from the alignement of the kinks or shifts. The lines are in many cases parallel to the $\{10\bar{1}0\}$ faces, but often show very complicated bends and curves, and do not necessarily follow the crystallographic directions. In Fig. 26, the directions of these lines observed in this study are schematically illustrated.

There is no difference, except the existence of the lines, between the surface patterns of single crystals and the crystals having these lines. The growth patterns on both sides of each line are common and not independent.

As a result of observations of these lines under the phase contrast microscope, it is found that (1) there is always a level difference between both sides of each line and the level difference is from a few to a few thousand angstroms, (2) there are evidences of further growth after the formation of the lines, (3) thick growth layers can

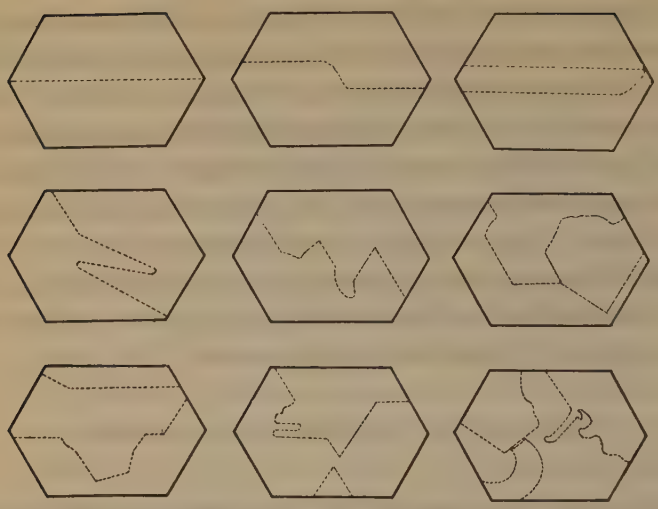

Fig. 26. Orientations of twin boundaries observed on the basal plane of hematite crystals. Dotted lines show twin boundaries.

cross the line forming kinks or shifts where they meet it while thin growth layers can not cross the line and stop their spreading at the line (Fig. 27), (4) growth layers, growth spirals and etch patterns which have triangular form show opposite orientations on the opposite side of the line, irrespective of the directions and the nature of the lines (Fig. 28a, b).

From these facts, it can be said that (1) the line is a twin boundary and the both sides of each line are in the relation of contact twinning with $\{10\bar{1}0\}$ as composition plane, (2) the line is formed during growth and further growth takes place after the formation of the lines, (3) the line is formed through the process that a part of a crystal growing as a single crystal slips down relative to the other part of the crystal, (4) the amount of this fault or slip is considered to be a fractional multiple of a unit cell height, since thin layers can not cross the line.

The previous explanation of the mechanism of contact twin for-

Fig. 18a. Piled up triangular growth layers observed on a crystal from Ayumikotan. Positive phase contrast. ×150.

Fig. 18b. High magnification positive phase contrast photomicrograph of the central part of piled up triangular layers. An interlacing pattern is observed. ×850.

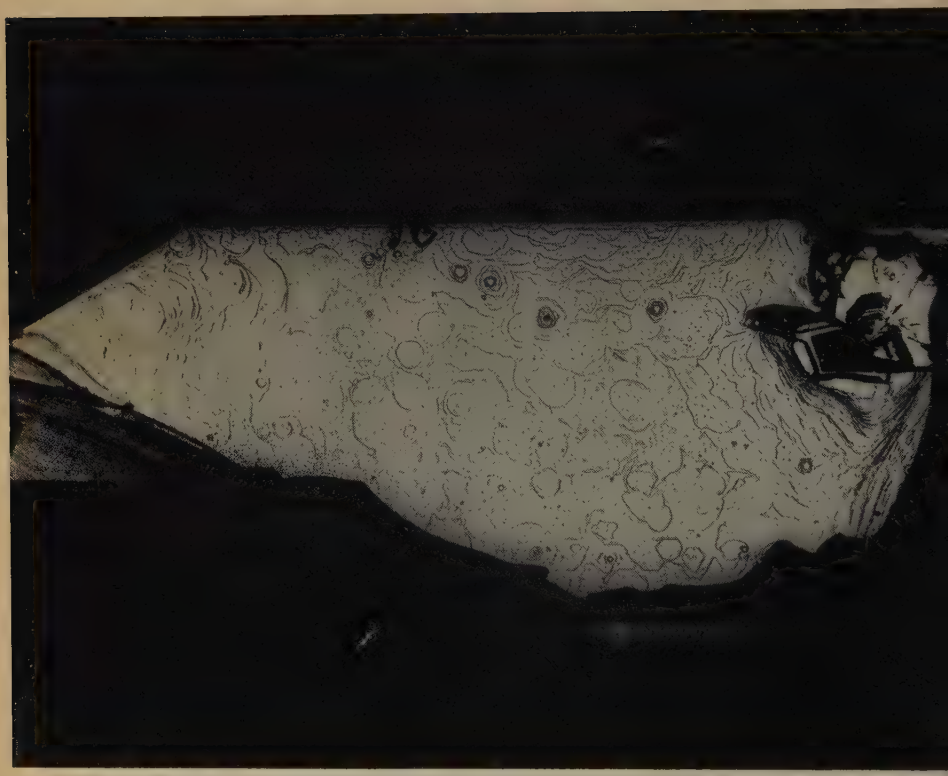

Fig. 19. Ordinary photomicrograph of the surface structure of a basal plane which received natural etching. The Azores Islands. ×10.

Fig. 21. Positive phase contrast photomicrograph of flat-bottomed depressions formed by etching. The Azores Islands. ×250.

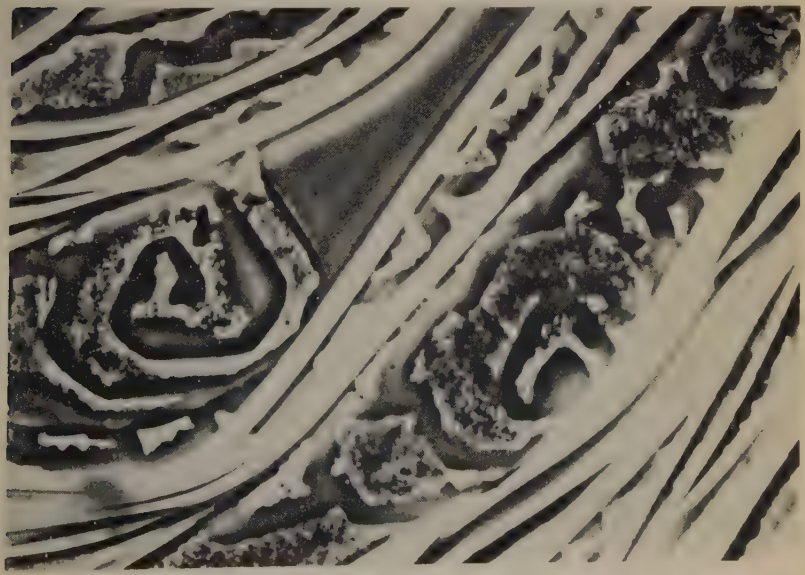

Fig. 22. Positive phase contrast photomicrograph of naturally etched spirals. The Azores Islands. ×400.

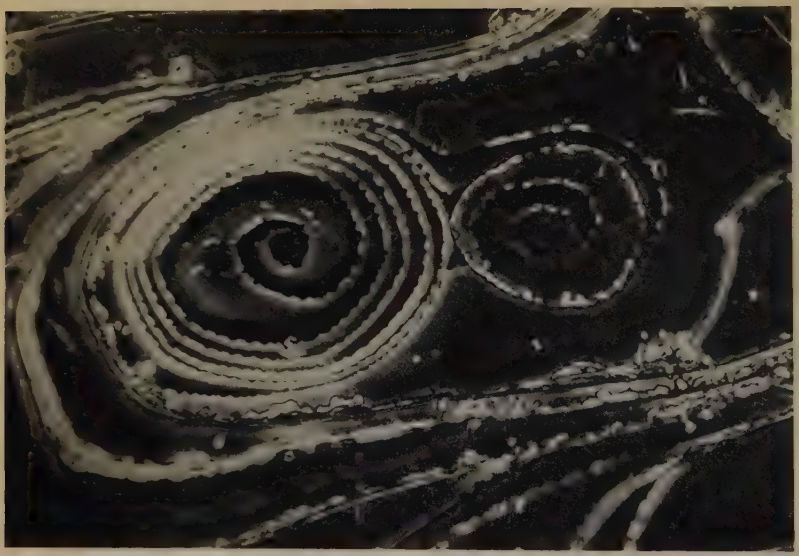

Fig. 24. Positive phase contrast photomicrograph of depression spirals formed by natural etching. The Azores Islands. ×600.

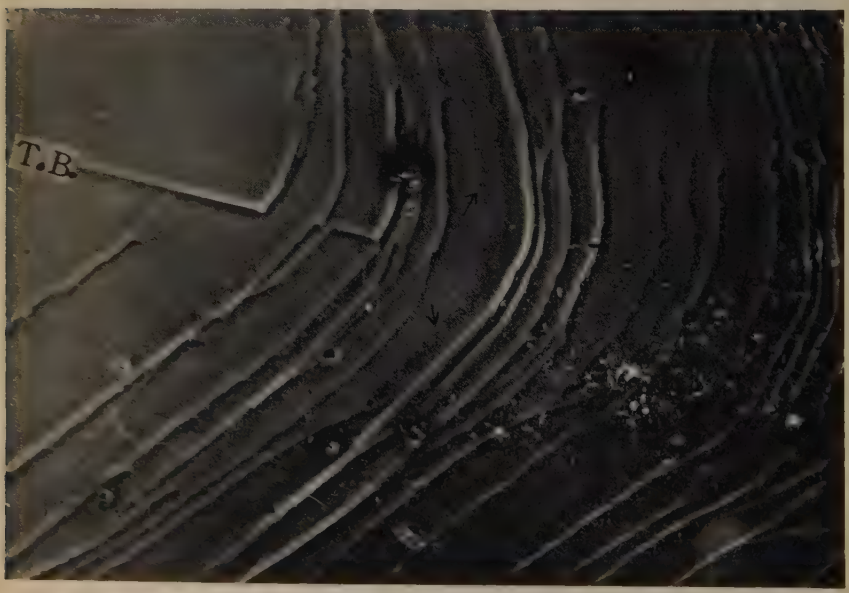

Fig. 27. Positive phase contrast photomicrograph showing a twin boundary. T. B. shows the position of twin boundary, and arrows show small triangular growth layers which are oppositely orientated on both side of the twin boundary. Gihofuji. ×270.

Fig. 28a, b. Two examples showing opposite orientation of triangular features on both sides of the twin boundaries. Positive phase contrast. The Azores Islands. ×270.

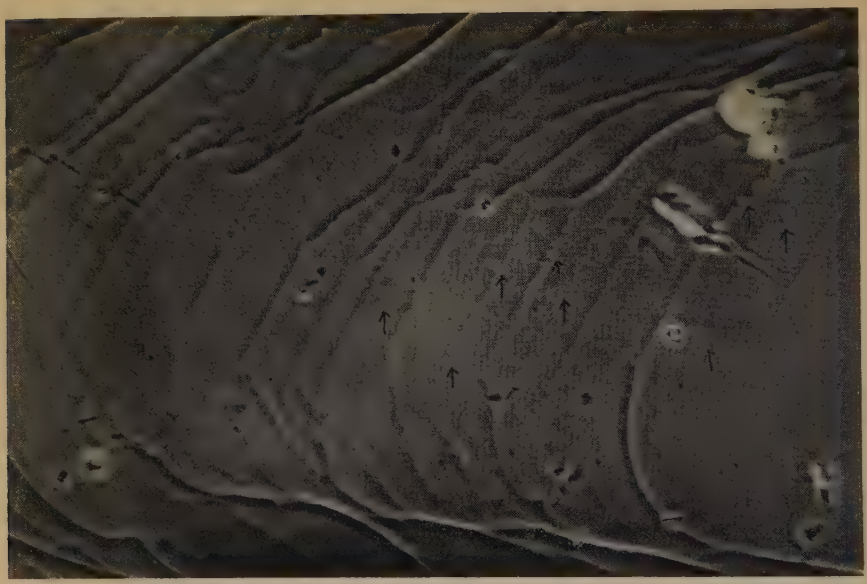

Fig. 30. Positive phase contrast photomicrograph showing twins formed by stacking fault during growth. Arrows show triangular projections. Gihofuji. ×270.

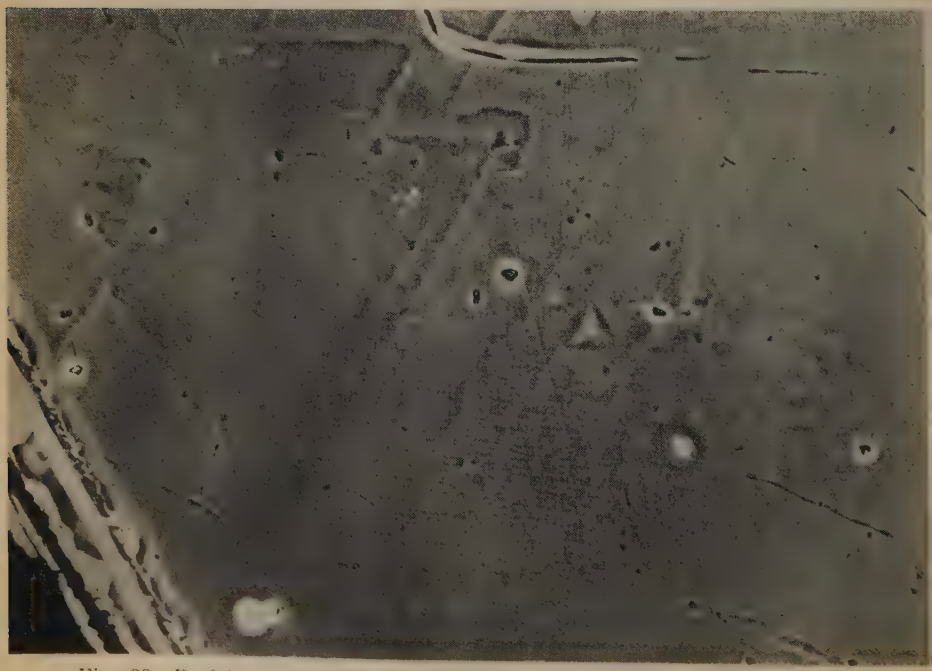

Fig. 33 Positive phase contrast photomicrograph showing polysynthetic twinning formed by stacking fault during growth. Saganoshima. ×300.

mation which is widely accepted is that two single crystals join together in twin position while they are growing. In the case that the main growth plane and the composition plane of twinning are the same, such as in the case of alum, this explanation is reasonable, since the probability of joining is fairly high in such a case. However, if these two planes are not the same and no growth layers develop on the surface of contact twin plane as in the case of hematite (main growth takes place on the basal plane and practically no growth layers develop parallel to the $\{10\bar{1}0\}$ face which is the composition plane of the twin.), the probability of joining of two single crystals on the $\{10\bar{1}0\}$ plane is considered to be negligibly small.

As already explained, one unit cell of hematite contains six layers of Fe-O-Fe parallel to the basal plane. Triangles consisting of three oxygen atoms have opposite orientations in successive layers. Therefore, if fault or slip, the amount of which is a fractional multiple of a unit cell, takes place during growth and growth continues after the formation of fault or slip, both sides of the fault plane will be in the relation of twinning, as schematically shown in Fig. 29. It

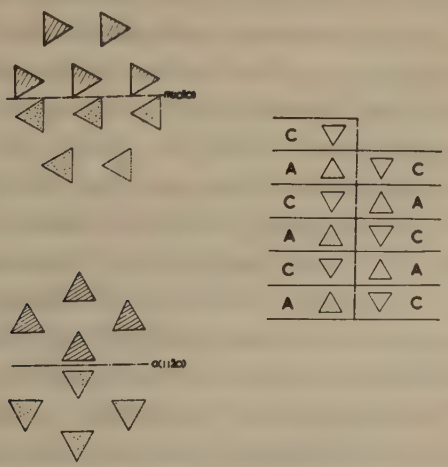

Fig. 29. Schematic figures showing twin structure.
Left: plane. Right: profile.

seems that the observed facts concerning the twin boundaries can be more satisfactorily explained on the basis of this mechanism than by the previous explanation.

(B) *Twinning due to stacking fault*[23]

It has been theoretically considered for long time that the polysynthetic twinning such as of plagioclase has been formed by successive stacking fault which has taken place during growth. However, no direct observations or proof for the twinning due to stacking fault have been reported so far. Several clear evidences of the twinning due to stacking fault are found on hematite in this study, which will be described briefly in this section.

The orientations of growth layers, or growth spirals having triangular forms are always the same on the whole surface of a crystal face, if the crystal is single, and are opposite on the opposite side of a twin boundary, in the case of contact twin. In the latter case too, their orientations are the same on the whole surface of each individual of the twin. However, as a result of cautious observations on the surface structures of a large number of hematite crystals with the phase contrast microscope, three examples in which two sets of oppositely orientated triangular layers appear on one surface have been found on a few crystals. These are as follows.

1. On one crystal from Gihofuji, small triangular projections occur along the edges of thin triangular growth layers, as shown in Fig. 30. The orientation of these triangular projections is opposite to that of the main triangular growth layers which cover the whole surface. If these projections are observed under high magnification using phase contrast, the relation which is schematically shown in Fig. 31 can be observed between the projections and the main growth layers. As clearly seen in this figure, the thickness of the projections is bigger than that of a main growth layer and is a fractional multiple of the latter, because there is a level difference between the surface of the projection and the layer B in Fig. 31 while the layer A completely cover the projec-

tion. Since the height of a main growth layer is about 14Å., one unit cell high, the above described level difference is less than the height of one unit cell. Therefore, it is considered that stacking fault must have taken place between the projection and the substratum when the former settle down on the growing surface. As the triangular projections have opposite orientation to the main growth layer, these two sets of growth layers are in the relation of twinning, the twinning plane of which is the basal plane. Therefore, this twinning is considered to be formed by stacking fault during growth.

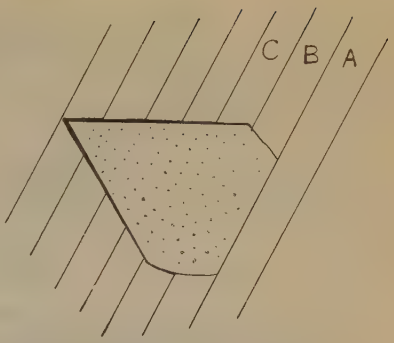

Fig. 31. Schematic figure showing the relation between a triangular projection and the main triangular growth layers. Dots show the surface of the triangular projection. Right is the higher side.

2. Nearly whole the surface of a crystal from Saganoshima is covered with a triangular spiral pattern having step height of 7Å. There are triangular islands and tongue-like terraces having triangular form on the same surface. Orientation of the triangular islands and terraces is opposite to that of the triangular spiral, which suggests that these two features are in the relation of twinning parallel to the basal plane. It is observed that there is a small level difference between the top surface of the terraces and the last layer of the spiral layers which are intercepted by the former, as schematically shown in Fig. 32. Therefore, this level difference must be less than 7Å., and possibly either 2.3Å. (one layer) or 4.6Å. (two layers in the unit cell). As stacking fault of two layers missing will not produce twin relation, the level difference must be 2.3Å. From this consideration, it can be concluded that this twinning is formed by stacking fault of one layer missing.

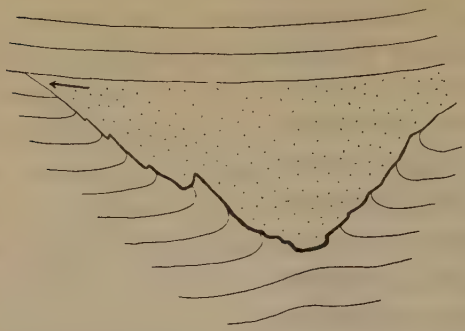

Fig. 32. The relation between a tongue-like terrace (originally a triangular island) and triangular spiral growth layers, dots showing the surface of the former. Top of the figure is the higher side. An arrow shows the final discontinuity between two features.

3. It is observed on one crystal from Saganoshima that two sets of triangular growth layers which are oppositely orientated to each other are superimposed, as shown in Fig. 33. This is a kind of polysynthetic twinning in the order of a unit cell. This polysynthetic twinning is considered to have been formed by stacking fault which took place repeatedly during growth of the crystal.

Since successive layers in the unit cell are oppositely orientated, it is easily undersood that the twinning parallel to the basal plane can be produced by one or odd number of layers missing from the normal stacking sequence. The above described three examples clearly show that this kind of stacking fault took place while the crystal was growing and that twinning structure has been formed through this mechanism. Therefore, it can be said that the twin parallel to the basal plane can be formed by stacking fault during growth.

Although the twin described here is not the twin in usual sense of terminology, it is certainly twin in its nature. In these cases, twinning takes place in the order of a unit cell or a fraction, instead of a crystal body. In the writer's opinion the meaning of twinning should be extended to this order, and this has actually been proposed by Ito[12] in his twin space groupoid theory.

Conclusion

Studies on crystal growth have rapidly progressed since the birth of Frank's spiral growth theory. Development in the methods of observations and measurements, such as phase contrast microscopy, multiple-beam interferometry, etc., has made possible to observe the phenomena concerning crystal growth or etching with the accuracy of the order of one unit cell or a fraction. It has also made possible to observe directly the existence and behavior of internal imperfections of crystals, such as dislocations, impurities, etc., since they will disclose themselves onto the surface through the process of crystal growth or etching. Therefore, it is now possible to argue the mechanism of crystal growth, etching as well as the behavior of internal imperfections in terms of unit cell or minimum constituent of the unit cell, on the basis of surface topographic observations of crystal faces. Since different surface structures of crystal faces will be formed under different crystallization conditions, it is also possible to know the difference of crystallization condition by comparing the characteristics of the surface structures of crystal faces.

In this paper, it is described what kinds of informations can be obtained by the surface topographic studies of crystal faces, by introducing the results of studies on hematite crystals from nine localities. Surface structures of crystal faces of hematite are observed with a reflecting and a phase contrast microscope, and the step heights of growth layers as well as the other surface features are measured precisely with multiple-beam interferometry and fringes of equal chromatic order. Informations obtained in such studies are as follows.

1. Mechanism and process of crystal growth of hematite;
2. Supersaturation conditions of crystal growth in each locality;
3. That the unit of growth is not one unit cell, but the minimum constituent layer of the unit cell;
4. Movement of dislocations after the cessation of growth and the stress history of crystals;

5. Predict of possibility of polytypism in hematite;
6. Mechanism of natural etching, a new interpretation;
7. Crystallization environments deduced from the degree of etching;
8. A new interpretation for the mechanism of contact twin formation;
9. The first direct observation of twinning due to stacking fault during growth, and its structural interpretation.

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URANOTHORITE FROM NAÉGI, GIFU PREFECTURE

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Abstract

Uranothorite from Naégi, Gifu Prefecture occurs as small grains in placers. Colour: Yellowish or reddish brown. Sp. gr.: 4.30. *n:* about 1.68. The result of chemical analysis of the sample from Nameri, Kitsumizawa follows, CaO 1.16, PbO 0.98, Al_2O_3 1.84, Fe_2O_3 2.54, Ce_2O_3 etc. 1.89, ThO_2 58.17, UO_2 9.05, SnO_2 0.26, TiO_2 0.02, SiO_2 11.89, P_2O_5 0.59, $H_2O(+)$ 7.10, $H_2O(-)$ 4.98, total 100.47%. The main features of the specimen imply that it is a metamictized mineral belonging to the uranothorite-thorogummite series.

Introduction

The occurrence of a reddish brown radioactive mineral akin to orangeite in placer samples from Naégi district, Gifu Prefecture was first found by Mr. H. Awazu in 1913. In 1931, the mixture of the mineral and monazite which was collected by him was investigated chemically by Drs. K. Kimura and Y. Miyaké, and was found to be a member of the thorite group near (Th, U) $O_2 \cdot SiO_2 \cdot 3H_2O$ in chemical composition, where $ThO_2 : UO_2 = 9 : 4$[3]. It was proposed to call the mineral enalite after the province name of the locality. No other description of the mineral has hitherto been published.

The writer has studied on the brown coloured radioactive mineral which was collected from the same district and revealed that the mineral belongs to the uranothorite-thorogummite series.

Occurrence

There are many placer deposits in Naégi district, Gifu Prefecture, which is one of the most famous localities producing rare earths

minerals in Japan.

The geology of the area was already reported by Dr. H. Shibata[4]. The district consists of quartz porphyry, granite porphyry, biotite granite, Tertiary formation and alluvial bed. Granite intrudes quartz porphyry and granite porphyry, and is considered to be of Cretaceous age. The granite is classified into three types; (1) fine-grained granite (Naégi type), (2) coarse-grained granite (Kerokubo type) and (3) porphyritic granite (Shiroyama type). Numerous drusy pegmatites are distributed in the Naégi type granite, and contain various kinds of minerals such as cassiterite, monazite, enalite, fergusonite and naegite. Enalite or uranothorite occurs in placer samples in the alluvial bed which overlies the Naégi type granite, and is supposed to have been derived from those drusy pegmatites and the Naégi type granites.

The writer collected and examined several heavy concentrates from the following localities: (1) Ichinosawa-gawa, (2) Kôketsu-yama, (3) Kitsumi-zawa, (4) Inari-dani, Kitsumi-zawa, (5) Yunoshima-gawa, (6) Jigoku-dani, (7) Nameri, Kitsumi-zawa.

Uranothorite was abundant in the last three samples, and the analysed sample was separated from the heavy concentrates from Nameri in which the mineral was particularly abundant.

The principal minerals in the heavy concentrates found from all of the areas from which samples have been examined include topaz, cassiterite, magnetite, wolframite, naégite, fergusonite, monazite, biotite, zircon, tourmaline, red garnet, samarskite and limonite. Sapphire was present in small amounts in one sample from Kitsumi-zawa.

Description of uranothorite

Uranothorite from Nameri is particularly abundant in the 20 to 42 meshes fraction of samples. It occurs mostly in small grains of which the central parts are in general somewhat darker than the remaining portions.

There is considerable variation in colour and it is difficult to identify them exactly. They range from yellowish brown to reddish brown, and it is believed the paler colour is the result of metamictization or hydration. The specific gravity is 4.30. The indices of refraction are about 1.68, and the birefringence is extremely low.

Chemical composition

The heavy mineral concentrate from Nameri was sized into three fractions, 32-42, 42-60 and 60-80 meshes and each fraction was dressed roughly with a magnetic separator. Uranothorite is moderately paramagnetic with a susceptibility decidedly less than that of monazite, and as a result the mineral was fairly easily separated from the associated monazite.

Almost all of the uranothorite was concentrated in the nonmagnetic fraction with quartz, topaz, cassiterite and naegite, all of which are nonmagnetic or diamagnetic. This concentrate was then fractionated in Thoulet solution and acetylentetrabromide and subsequently hand-picked under the binocular microscope. Thus a nearly pure sample of the mineral was prepared and analyzed. Spectrochemical test of the sample revealed that thorium, uranium and silicon are the main constituents, iron, aluminium, calcium, rare earths and phosphorus are the small contituents and tin and lead are the minor elements of the sample.

X-ray fluorometric analysis revealed that the following rare earths are present: Ce, La, Nd, Sm, Gd, Dy, Er and Y.

The outline of the procedure of quantitative chemical analysis is as follows.

After the ignition loss was determined, the material was fused with sodium carbonate and digested with hot water. The residue was treated by sulphuric acid and SiO_2 and SnO_2 were determined. ThO_2, rare earths, Fe_2O_3, CaO and MgO were determined on the filtrate from silica. R_2O_3 group elements were separated from CaO and MgO by ammonium hydroxide, then ThO_2 and rare earths were

precipitated by oxalic acid, and ThO_2 was determined by hexamine method. P_2O_5, Al_2O_3 and UO_2 were determined from the first filtrate. The results are summarized in Table 1, Column 1.

Table 1. Chemical analysis of uranothorite from Naégi.

1		2		
CaO	1.16%	O	7.28	8.96
MgO	tr.			
MnO	tr.	OH	8.72	1.68
PbO	0.98			7.04
Al_2O_3	1.84	Si	2.16	4 4.00
Fe_2O_3	2.54	P	0.08	
Ce_2O_3 etc.	1.89	Ca	0.23	0.27
ThO_2	58.17	Pb	0.04	
UO_2	9.05	Al	0.39	0.86
SnO_2	0.26	Fe^{3+}	0.34	
TiO_2	0.02	Ce^{3+}	0.13	
SiO_2	11.89	U^{4+}	0.40	2.78
P_2O_5	0.59	Th	2.38	
$H_2O(+)$	7.10	H_2O	3.16	
$H_2O(-)$	4.98			
Total	100.47%			

1. Uranothorite from Nameri, Kitsumizawa, Naégi. Analyzed by T. Kato (1957).
2. Atomic ratios.

X-ray powder data

X-ray powder diffraction patterns, obtained with a Norelco diffractometer, were presented in Table 2, with those for anhydrous synthetic $ThSiO_4$ by C. Frondel[2] for comparison. The two patterns are virtually identical. Moreover, cell dimensions of the Naégi material, a_0 7.18Å and c_0 6.27Å, are close to those of thorite or uranothorite. The diffraction lines were rather diffused, implying the metamictization or hydration in a considerable grade.

Table 2. X-ray powder data for uranothorite
(CuKα radiation)

hkl	1		2	
	d	*I*	*d*	*I*
011	4.73Å	60	4.69Å	90
200	3.59	100	3.56	100
121	2.85	50	2.84	70
112	2.67	80	2.66	80
220	2.53	20b	2.52	50
031	2.24	40	2.22	5
013	2.01	30	2.01	50
321	1.901–1.886	30	1.89	60
312	1.835	60	1.84	100

1. Uranothorite from Naégi. 2. Anhydrous synthetic tetragonal $ThSiO_4$[2]. b: diffused line.

Thermal data

Differential thermal analysis showed a gradual loss of water at 100° to 250°C., exothermic peaks at 480°C. and 785°C. and a small but sharp endothermic one at 830°C. The last peak will be interpreted as the indication of the loss of OH.

Infrared absorption data

Infrared absorption curves showed several absorption maxima at 2.70, 6.20, 6.70, 7.2 and 8.7μ. The molecular water absorption at 6.20μ was greater than the OH absorption at 2.70μ. The spectra caused by SiO_4 and UO_2 molecules in the region of 9.5 to 10.5 and 13 to 16μ, respectively, were observed but not so distinct.

Discussion of the results

The results of chemical analysis and X-ray examination show that the mineral is akin to a metamictized uranothorite or orangeite. The Th/U ratio is rather similar to that of common uranothorite.

Taking into consideration the cell content of four molecules, which has been derived from the obtained chemical composition, cell dimensions and specific gravity and on assumption that $(OH)_4$ substitutes for SiO_4 for compensating the deficiency of SiO_4 and that OH substitutes for O for compensating the charge unbalance due to a substitution of R^{2+} and R^{3+} ions for R^{4+} ion, the chemical composition in terms of atomic proportion was calculated as given in Table 1 Column 2. The composition is represented by the formula $(R^{4+}\ R^{3+}\ R^{2+})_{0.9}\ [Si,\ P(O,\ OH)_4]_{1-0.44}\ (OH)_{1\times 0.41}\ 0.8\ H_2O$. It is similar to the formula $(Th, U)\ (SiO_4)_{1-x}\ (OH)_{4x}$ developed by Frondel[1) 2)] for the thorite-thorogummite group minerals. The mineral from Naégi may be considered as an intermediate member of the uranothorite-thorogummite series.

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MINERALOGICAL ABSTRACTS

FROM

THE SCIENTIFIC PAPERS PUBLISHED IN JAPAN

Apparatus and Techniques

30001. **Sato (Mitsuo):** *Rapid analysis of sphalerite by use of ion exchange resin and volumetric method.* Kobutsugaku Zasshi, **4**, 293–298 (1959).

Details are given of utilizing ion exchange resins and volumetric method for determining Zn, Fe, Cd, Mn, Cu and S in sphalerite. In comparison with ordinary method, the process developed is simpler, and an analysis of one specimen can be carried out within three days at extremely low cost. Separation of the elements are better and the amount of samples required for the analysis is only about 0.1 g.

Clay Minerals

30002. **Yamamoto (Tutomu):** *Rôseki clays from Mitsuishi, Okayama Prefecture.* Kobutsugaku Zasshi, **4**, 277–292 (1959).

Results of X-ray investigation, thin section observation, chemical analysis and firing test for Rôseki clays from Daiyama, Mitsuishi are described. From X-ray powder diagrams, main constituent minerals of these clays are found to be diaspore, boehmite, kaolinite, pyrophyllite, sericite and quartz. Results of chemical analysis, along with X-ray data, are utilized to establish the paragenesis of the constituent minerals. Pyrophyllite, kaolinite, diaspore and boehmite are paragenetic with each other, while sericite is scarcely found coexisting with the other minerals except quartz. Paragenesis of quartz with the other minerals except sericite and pyrophyllite is also rare. Clays with high SiO_2 and Al_2O_3 content are found to be high in refractoriness, whereas those with the chemical composition equivalent to that of the eutectic point of Al_2O_3–SiO_2 system are low.

Crystal Structure of Minerals

30003. **Takano (Yukio) & Takano (Kotoyo):** *The problem of the stability of reciprocal main axes in polysynthetic twin.* Jour. Jap. Asso. Min. Petro. & Econ. Geol., **43**, 194–202 (1959).

The relations between the twinning axes and the reciprocal main axes are discussed, and a conception of the reciprocal lattice for clear and accurate descriptions of twinning is proposed.

Economic Minerals and Ore Deposits

30004. **Watanabe (Takeo):** *The minerals of the Noda-tamagawa*

mine, Iwaté Prefecture, Japan. I. *Note on geology and parageneses of minerals.* Mineralogical Journal 2, 408-421 (1959).

The ore deposits of the Noda-Tamagawa mine have become famous for their wealth of mineral species, the production of high grade manganese ores, and also the recent discovery of uranium ores. More than seventy minerals have been found in this mining area including such rare minerals as pyrochroite, manganosite, vredenburgite, yoshimuraite (a new mineral of Ba, Sr, Mn, Ti-silicate), etc.

The ore deposits of this mine may be classified into the following types:

(A) The contact-metamorphosed bedded manganese deposits in matamorphosed roof pendant in the batholithic mass of granitic rocks.

(B) (1) The uranium-bearing veins.
(2) The cobalt-nickel-molybdenum-bearing uranium deposits associated with pelitic hornfels.

(C) Pyrometasomatic copper-bearing uranium deposits associated with pelitic hornfels.

(D) Gold-silver-bearing quartz-arsenopyrite veins.

Among them manganese deposits are economically the most important ones. The geology and ore deposits of the mine are briefly described. The mineral parageneses of ores and country rocks are shown in Tables 1 and 2.

Experimental Mineralogy

30005. **Fukui (Tadaoki):** *Mineralogical study on the stone in glass.* Mineralogical Journal, 2, 355-374 (1959).

Morphological, optical and X-ray properties of several stones in glass were described and considerations were made of the geneses of these stones.

It has been found that the difference in the variety of the stones arises from the difference in compositions of molten glass itself and/or of refractory bricks. In addition, foreign materials which have been captured in the molten glass also affect the character of stones.

The writer found new occurrences of aegirine, celsian, hercynite and spinel in stones.

30006. **Hayashi (Hiroshi) & Naka (Shigeharu):** *Synthesis of cobalt olivine.* Repts. Government Industr. Research Inst., Nagoya, **9**, 141-146 (1960).

Cobalt olivine and olivine of $(Co, Mg)_2SiO_4$ system have been synthesized from a mixture of chert, CoO from cobalt nitrate and MgO from magnesium chloride. The mixture of raw materials was calcined in a platinium crucible at temperatures between 1350 and 1500°C. for one hour. The product was ground again, shaped, and then subjected to temperatures between 1350 and 1500°C. for 1-5 hours. The X-ray pattern of the product with the composition of Co_2SiO_4 showed a good agreement with that of iron-olivine, confirming that the product was a cobalt olivine. The same

was true of the product with the composition of $(Co,Mg)_2SiO_4$, indicating the presence of continuous solid solution between Co_2SiO_4 and Mg_2SiO_4. SiO_2 added in excess of Co_2SiO_4 produced cristobalite together with olivine; no enstatite structure being formed. CoO added in excess of Co_2SiO_4 produced CoO.

30007. **Hukuo (Ken-iti)**: *Constitution of the magna china.* Bull. Nagoya Inst. Techn., 11, 202–205 (1959).

Artificial enstatite synthesized from sea-water magnesia and quartz sand is mixed together with clays and chert as plasticizers, fired and then glazed to make magna china. X-ray and microscopic observations have been made for the magna china without glaze. Judging from the X-ray diffraction pattern of the body, its constituent minerals are cristobalite, proto-enstatite, quartz, and clino-enstatite. As compared with minerals (proto-enstatite, small amount of quartz and tridymite) found in artificial enstatite used as a starting material, disappearance of tridymite and formation of cristobalite are observed. Under the microscope, coarse grains of quartz in the starting mixture are found remaining neither reacted nor transformed, whereas those of less than 5 μ in size are transformed to cristobalite. Alumina and silica of clays react with artificial enstatite to form a glass phase.

30008. **Minato (Hideo)**: *Melilite crystal in the cavity of blast-furnace slag.* Mineralogical Journal, 2, 422–426 (1959).

Idiomorphic crystals of melilite (A) collected from cavities of blast-furnace slag at the Yawata Iron Works are described. They are higher in gehlenite content than the phenocryst melilite (B) in the neighbouring massive slag.

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Ig. loss	$H_2O(-)$	Total
A	23.25	1.21	23.47	1.97	4.45	40.58	0.81	non	100.79
B	29.05	0.53	20.87	2.00	6.64	40.20	0.93	non	100.27

30009. **Nishimura (Shin'ichi)**: *Extraction of thorium and Uranium from monazite (Refining by solvent extraction).* Mem. Coll. Sci., Univ. Kyoto, Ser. B, 26, 173–191 (1959).

An economic manufacturing technique is described for the production of Th- and U-salts from monazite sand by solvent extraction.

30010. **Okada (Kokichi)**: *Thermal study on some γ type ramsdellites.* Jour. Jap. Asso. Min. Petro. & Econ. Geol., 43, 229–238 (1959).

The X-ray powder diagram of the manganese dioxide mineral from the Iwasaki manganese mine, Aomori Prefecture, is simillar to that of γ-MnO_2I described by Cole, Wadsley and Walkley in 1947.

Geochemistry

30011. **Yamaoka (Kazuo)**: *On the occurrence and the minor elements of magnetite and hematite from the Sambagawa crystalline schist in Shikoku.* Jour. Jap. Asso. Min. Petro. & Econ. Geol., 43, 297–308 (1959).

Magnetite and hematite from the cupriferous iron sulfide deposits were collected in Shingu, Shiratori, Sazaré and Kotsu mines, which are located in the Sambagawa crystalline schist zone. The distributions of the minor elements in the crystals are studied.

Mineral Data

30012. **Banno (Shohei):** *Aegirine-augite from crystalline schists in Shikoku.* Jour. Geol. Soc. Jap., **65**, 652–657 (1959).

Aegirine-augites were separated from two host rocks in the metamorphic area where biotite is stable in pelitic schists. One from aegirine-augite-alkali amphibole-garnet-apatite-albite-quartz schist collected at Hodono near Besshi, another from aegirine-augite-magnesioriebeckite-bearing schist collected at Bizan near Tokushima, respectively. Chemical compositions are given: (1) from Hodono; SiO_2 51.80, Al_2O_3 3.61, TiO_2 0.06, Fe_2O_3 16.49, FeO 2.03, MnO 0.96, MgO 6.98, CaO 10.86, Na_2O 7.01, K_2O 0.13, $H_2O(+)$ 0.43, $H_2O(-)$ 0.08, P_2O_5 0.02, total 100.46 (Analyst: H. Haramura), (2) from Bizan: SiO_2 52.47, Al_2O_3 6.98, TiO_2 0.10, Fe_2O_3 17.39, FeO 1.25, MnO 1.27, MgO 4.88, CaO 6.87, Na_2O 8.51, K_2O 0.28, $H_2O(+)$ 0.43, $H_2O(-)$ 0.08, P_2O_5 0.01, total 100.24 (Analyst: H. Haramura). Molecular compositions calculated by the author's method are (1) $Ac_{46}Jd_{23}Di_{30}$ and (2) $Ac_{47}Jd_{23}Di_{30}$. Jadeite molecule in the alkali-pyroxenes tends to decrease with increasing metamorphic grade. They never coexist with epidote nor with chlorite.

30013. **Banno (Shohei):** *Finding of paragonite from the Besshi District, Shikoku, and its paragenesis.* Jour. Geol. Soc. Jap., **66**, 123–130 (1960).

Paragonite was found from kyanite-amphibolite, garnet-amphibolite as well as from hornblende schist in the anounced district. The mineral was separated, and analysed giving the following result: SiO_2 46.20, Al_2O_3 39.58, TiO_2 0.30, FeO 0.3, MnO<0.02, MgO 0.14, CaO<0.1, Na_2O 6.76, K_2O 0.62, $H_2O(+)$ 4.81, $H_2O(-)$ 0.10, P_2O_5 0.16, total 99.88. Some critical data on its optical and X-ray properties are also presented.

30014. **Banno (Shohei):** *Glaucophane and garnet from the Kotsu District, Shikoku.* Jour. Geol. Soc. Jap., **65**, 658–663 (1959).

Two glaucophanes and a garnet were separated from the crystalline schist at the Kotsu mine, and analysed. The host rocks are (1) glaucophane-epidote-chlorite-quartz-albite schist, and (2) glaucophane-epidote-chlorite-garnet-albite-quartz schist; both, according to the author, belong to glaucophane schist facies. The results of chemical analyses (analyst: H. Haramura) are given as follows. Glaucophane from the rock (1): SiO_2 54.56, Al_2O_3 8.29, TiO_2 0.23, Fe_2O_3 7.94, FeO 10.31, MnO 0.13, MgO 8.74, CaO 0.81, Na_2O 6.71, K_2O 0.14, $H_2O(+)$ 2.18, $H_2O(-)$ 0.07, P_2O_5 0.01, total 100.12, glaucophane from the rock (2): SiO_2 54.88, Al_2O_3 9.86, TiO_2 0.87, Fe_2O_3 4.35, FeO 12.02, MnO 0.14, MgO 7.69, CaO 1.95, Na_2O 5.62, K_2O 0.09, H_2O

(+) 2.22, H_2O(−) 0.13, P_2O_5 n. d., total 99.82. Optical properties are also given. Garnet from the rock (2): SiO_2 36.05, Al_2O_3 20.82, TiO_2 1.37, Fe_2O_3 1.43, FeO 22.73, MnO 4.76, MgO 0.77, CaO 11.28, Na_2O tr., K_2O tr., H_2O(+) 1.16, H_2O(−) 0.00, total 100.37; molecular percentage is $Al_{52}Sp_{11}Py_3Gr_{30}An_3$.

30015. **Hariya (Yu):** *A new find of groulite $HMnO_2$, in Japan.* Jour. Fac. Sc., Hokkaido Univ. Ser. 4, **10**, 255-267 (1959).

Platy crystals of groulite were found in the Pirika mine, Hokkaido, associated with manganite, quartz, barite and limonite. Specific gravity is 4.183 at 4°C. The presence of Mn is confirmed by microchemical and X-ray fluorescence analyses. Very strong anisotropism distiguishes the mineral from manganite. D. T. A. curve shows two endothermic peak at 395°C. and 980°-1020°C. Thirty three X-ray powder lines were observed and among them the following three are of strong intensity; d(Å) =4.19, 2.37, 2.67.

30016. **Kato (Toshio):** *Heulandite and chabazite from Hashikakézawa, Chichibu Mine, Saitama Prefecture.* Kobutsugaku Zasshi, **4**, 299-306 (1959).

Heulandite and chabazite crystals (2.5 cm. and 1 cm., respectively) occur in a skarn druse at Hashikakézawa, Chichibu Mine, associated with garnet, epidote, axinite and calcite.

(1) Heulandite: α=1.503, β= 1.504, γ=1.510, $2V$=(+) 74°, $r>v$. Crystal forms: b(010), c(001), t(201), m(110) and s($\bar{2}$01). Analysis gave, SiO_2 57.29, Al_2O_3 16.73, Fe_2O_3 0.13, CaO 6.36, SrO 0.85, K_2O 2.74, Na_2O 0.75, H_2O(+) 11.54, H_2O(−) 3.89, total 100.28.

(2) Chabazite: α=1.488, γ=1.490, $2V$=(±) 0°. Crystal forms; r(10$\bar{1}$1). Analysis gave, SiO_2 44.19, Al_2O_3 19.86, Fe_2O_3 0.28, MgO 1.56, CaO 8.61, SrO 0.15, K_2O 2.05, Na_2O 1.18, H_2O (+) 14.36, H_2O(−) 7.44, total 99.68.

X-ray diagram, thermal data and spectrographic analyses are given.

30017. **Kato (Toshio):** *Pyromorphite from the Yawa Tin Lode Mine, Burma.* Mineralogical Journal, **3**, 42-44 (1960).

Non-radioactive pyromorphite collected from the oxidized zone of cassiterite-quartz vein of the Yawa Tin Lode Mine: PbO 80.52, P_2O_5 16.18, As_2O_5 0.90, Cl 2.40, −O(=Cl) 0.56, total 99.44. The relative isotopic abundance of lead in the mineral falls in the range of ordinary lead of relatively young age.

30018. **Okamoto (Yohachiro), Sakurai (Kin'ichi) & Kato (Akira):** *Pyrophanite from Oyamada.* Kobutsugaku Zasshi, **4**, 307-309 (1959).

Morphological and X-ray data for pyrophanite from Oyamada, Aichi Prefecture in Japan were given. a_0=5.137Å, c_0=14.28Å. The results of X-ray fluorescence analysis show the presence of Mn, Ti and Fe (Mn : Fe=10 : 1).

30019. **Omori (Keiichi) & Seki (Toshikazu):** *Infrared study of some phosphate minerals.* Jour. Jap. Asso. Min., Petro. and

Econ. Geol., 44, 7-13 (1960).

The infrared spectra of xenotime and monazite from Ishikawa, Fukushima Pref., apatite from Kurokura, Kanagawa Pref., apatite from Duranga, Mexico, pyromorphite from the Matsuhodo mine, Miyagi Pref., vivianite from the Ashio mine, Tochigi Pref. and autunite from Grafton, New Hampshire, U. S. A. were studied by the Perkin-Elmer Model 21 double beam infrared spectrophotometer. All the spectra have broad bands caused by PO_4 molecules at 9 and 9.5 microns.

30020. **Sasaki (Akira):** *Variation of unit cell parameters in wolframite series.* Mineralogical Journal, 2, 375-396 (1959).

The variation of unit cell parameters in the wolframite series has been investigated on the specimens sythesized by fusion of various mixtures of $FeCl_2 \cdot 4H_2O$, $MnCl_2 \cdot 4H_2O$ and $Na_2WO_4 \cdot 2H_2O$. The results show that a_0, b_0 and c_0 increase almost linearly with increasing MnO content as follows: from $a_0=4.732$Å, $b_0=5.707$A and $c_0=4.965$Å in $FeWO_4$ to $a_0=4.834$Å, $b_0=5.758$Å and $c_0=4.999$Å in $MnWO_4$. Angle β varies also gradually from 90°00′ in $FeWO_4$ to 91°11′ in $MnWO_4$. However, it appears that the value of 90°00′ is maintained in the range from $FeWO_4$ to about $(Fe_{0.9}Mn_{0.1})WO_4$. The measurement has also been carried out on six natural specimens whose chemical data had been available. The unit cell parameters of these natural wolframites appear to follow the same variation diagram obtained with the synthetic specimens, although some numerical deviation are unavoidable. The differences between the result of chemical analysis and the composition determined by using the variation diagram are within the range of ±6 mol per cent.

30021. **Seki (Yotaro):** *Actinolite in the eastern part of the Kanto mountain.* Jour. Jap. Asso. Min. Petro. & Econ. Geol., 43, 179-184 (1959).

Glaucophanitic regional metamorphic terrain in the eastern part of the Kanto Mountains in the central Japan can be divided into the following two zones which are characterized by pale colored actinolite (I) and greenish blue actinolite (II) respectively. The latter is only found in the highest grade part of the terrain and the former is distributed in the non-spotted schists, phyllite and weakly metamorphosed Paleozoic formations. Chemical and optical data are as follows.

	I	II		I	II
SiO_2	56.03	50.55	α	1.623	1.6[illegible]
Al_2O_3	2.1	6.21	β	1.64[illegible]	1.661
Fe_2O_3	2.22	5.40	γ	1.[illegible]0	1.66[illegible]
FeO	8.97	11.58	2V	78°	6[illegible]°
MnO	0.23	0.32			
MgO	16.11	10.72	c/\z	21°	0°
CaO	10.28	9.77			
Na_2O	1.36	1.46			
K_2O	none	0.18			
$H_2O(+)$	2.42	2.89			
$H_2O(-)$	0.17	0.31			
Total	99.96	99.69			

30022. **Shido (Fumiko):** *Data on a tremolite and three actinolites.* Jour. Geol. Soc. Jap., 65, 563-564 (1959).

The specimens described are tre-

molite in limestone from Gouverneur, New York (analysed by H. Haramura), actinolite from Chester, Vermont, U. S. A., (analysed by H. Haramura), sp. gr.=3.080, and actinolite from Scotland (analysed by H. Haramura). Optical properties and X-ray powder diffraction data for the tremolite are also given. The author concluded, comparing the unit cell dimensions of the tremolite and the actinolite from Scotland, that the variation of the cell dimensions in the tremolite-actinolite series with the Mg-Fe^{2+} substitution is extremely small.

30023. **Shido (Fumiko) & Seki (Yotaro):** *Hornblende from the Kamuikotan metamorphic belt.* Jour. Geol. Soc. Jap., **65**, 673-677 (1959).

Chemical data on a typical hornblende from an epidote-hornblende schist with biotite in the southern part of the Kamuikotan metamorphic belt in Hokkaido are given. The specimen of the host rock was collected from Mitsuishi in an isolated small area of the crystalline schists. The chemical composition is as follows: SiO_2 42.89, Al_2O_3 13.95, TiO_2 0.75, Fe_2O_3 6.07, FeO 13.39, MgO 7.41, MnO 0.27, CaO 9.75, Na_2O 2.83, K_2O 0.85, $H_2O(+)$ 1.68, $H_2O(-)$ 0.00, P_2O_5 0.01, total 99.85 (Analyst: H. Haramura); optical properties, $\alpha=1.669$, $\gamma=1.691$, $2V_z=56°$, disp. distinct; X=yellow, Y=dull green, Z=blue-green, $Y=Z>X$, $c\wedge Z=25°$. The very high ferric iron content is remarkable.

30024. **Shimazu (Mitsuo):** *Potash feldspars in some metamorphic rocks.* Jour. Jap. Asso. Min. Petro. & Econ. Geol., **43**, 185-193 (1959).

Potash feldspars from the Akka metamorphic rocks and the granites are studied by optical and X-ray methods. Triclinicity in potash feldspars of the Akka metamorphic rocks shows a monoclinic character, while the potash feldspars from the other metamorphic terrains show low triclinicity. With the percentages of the albite molecule contained in alkali feldspars, the formation temperature of potash feldspars may be determined by Barth's method.

30025. **Tokuda (Taneki):** *The X-ray powder patterns and the lattice constants of natural cristobalites.* Mineralogical Journal, **3**, 1-8 (1960).

Three natural cristobalite specimens from different localities in Japan were prepared by treating the raw specimens with fluoboric acid. The sample obtained from "Beppu Hakudo" gave rather sharp X-ray powder patterns in which many of the lines in the region of back reflection which had first been described in the writer's previous paper were recognized again. The lattice constants of the sample are larger than those of the standard artificial cristobalite by 0.30%. This discrepancy is attributable to the simultaneous crystallization of a small amount of tridymite in the sample. The patterns of the other two natural specimens are rather obscure, but their spacings are in

agreement with the standard values within the experimental errors.

30026. **Watanabe (Takeo), Kato (Akira) & Ito (Jun):** *The minerals of the Noda-Tamagawa mine, Iwaté prefecture, Japan.* II. *Pyrochroite ore (Kimiman-kô) and its origin.* Mineralogical Journal, **3**, 30-41 (1960).

The manganese ore, locally called "Kimiman" or "Kibiman" by the miners at the Noda-Tamagawa mine, is composed essentially of pyrochroite [$Mn(OH)_2$] hitherto known as a rare mineral. More than 50,000 tons of the pyrochroite ore have been shipped from this mine for metallurgical uses since 1950. The ore consists mainly of fibrous pyrochroite pseudomorph after manganosite with small amounts of manganosite, galaxite, tephroite, rhodochrosite, barite and alabandite. The pyrochroite occurs in scaly aggregates. When fresh, it is white but when exposed in air its colour changes into brown to black. Extinction is parallel to the elongated fiber. Character of zone is positive, $\varepsilon=1.683$, $\omega=1.725$ and $\omega-\varepsilon=0.042$. The unit cell dimensions obtained from the powder data: $a_0=3.323$Å. and $c_0=4.738$Å. The pyrochroite ore is considered to be hydrothermal alteration product from the manganosite ore, which may have been formed as dissociation product from the rhodochrosite ore of sedimentary type during the period of contact metamorphism of granitic intrusion.

30027. **Yajima (Sumisaku):** *Metacinnabar from Sarawak and Japan, with reference to its stability relations to cinnabar.* Mineralogical Journal, **3**, 9-18 (1960).

The mode of occurrence of metacinnabar at the Gading mine, Sarawak, is described. It was identified by X-ray powder patterns which were in good accord with those of artificial metacinnabar. Occurrences of the mineral in Japan are summarized, and among them the oolitic texture and metacinnabar veinlet in the ore of the Nikô mine are noticeable. Although some pseudomorphs of cinnabar after metacinnaber have been described from Japan, the two minerals, in general, seem to have been precipitated independently from hydrothermal solutions.

30028. **Yoshimura (Toyofumi) & Yoshinaga (Mayumi):** *Barites from some manganese ore deposits in the Tamba mountain region.* Jour. Jap. Asso. Min., Petro & Econ. Geol., **44**, 1-6 (1960).

Barites with bright emerald green colour were found at five manganese ore deposits in Tamba mountain region, Kyoto Prefecture. All of them occur as isolated grains or minute veinlets in the massive chocolate-like ores.

The barite from the Kihara mine gave the following properties; $G=4.10$, $\alpha=1.636$, $\beta=1.637$, $\gamma=1.646$, $\gamma-\alpha=0.010$; $2V(+)=39°$. Its chemical composition is, SiO_2 1.05, Al_2O_3 and Fe_2O_3 3.01, MnO 0.69, CaO 2.81, MgO 0.16, BaO 57.96, SrO none, SO_3 32.10, ig. loss 1.86, total 99.64.

New Minerals

30029. **Kato (Akira):** *Ikunolite, a new bismuth mineral from the Ikuno mine, Japan.* Mineralogical Journal, 2, 397-407 (1959).

Ikunolite, $Bi_4(S, Se)_3$, a new mineral from the Ikuno mine occurs in ferberite-bismuth-bismuthinite quartz vein. It belongs to rhombohedral system with $a_{rh}=13.28$Å, $\alpha=18°00'$, $Z=1$ (or $a_0=4.15$Å, $c_0=39.19$Å, $Z=3$ in hexagonal lattice) and the space group is $R\bar{3}m$. Physical and optical properties are: lead grey in colour and dark grey in streak colour; hardness 2, very flexible; specific gravity=7.97 (calc.), 7.8 (meas.); perfect cleavage parallel to {0001}; anisotropic in the section diagonal to the basal cleavage and etched by HNO_3 and $FeCl_3$ solution. Chemical analysis gives $Bi_{3.79}(S_{2.76}Se_{0.24})_{3.00}$ close to $Bi_4(S, Se)_3$ with S: Se=92: 8. The sheet structure determined by single crystal method is closely related to the other rhombohedral chalcogenides of bismuth. Ikunolite resembles joseite A $[Si_4TeS_2]$ in structure, crystallography and optical properties and belongs to the same group of bismuth-chalcogenide minerals with Bi: (S, Se, Te)=4: 3.

Physical Properties of Minerals

30030. **Kawai (Naoto), Ito (Haruaki), Yasukawa (Katsumi) & Kume (Shoichi):** *Remnant magnetism of dehydrated iron hydroxides in sedimentary and metamorphic rocks.* Mem. Coll. Sci. Univ. Kyoto, Ser. B, **26**, 235-239 (1959).

When dehydrations of goethite and lepidocrocite were made in a magnetic field of specific direction by applying a pressure (2550 atm., 350°~400°C.), resulting α-hematite and γ-hematite were magnetized not along the magnetic field but approximately perpendicular to the field. The results will be useful for the interpretation of remnant magnetism of sedimentary and metamorphic rocks.

30031. **Kiriyama (Ryôiti) & Kawai (Shichio):** *Dielectric phenomena of smoky quartz, natural and X- and γ-ray irradiated.* Mineralogical Journal, 3, 19-29 (1960).

Dielectric dispersion of natural smoky quartz was observed in the audio-frequency region at about 400°C. The enthalpy of activation for the dielectric relaxation was about 50 kcal/mole in contrast with a value of about 20 kcal/mole for natural colourless quartz. By thermal bleaching, the enthalpy of activation falls to the value for natural colourless quartz.

Exposed to X-rays, the bleached quartz coloured again and the value of activation enthalpy recovered, and to γ-rays of about 10^5 to 10^7 r. in total dose, coloration also attained, but the effect was different from that by X-rays. A linear relation was found between the energies of activation and the logarithms of the total doses of irradiation.

Probable molecular mechanisms responsible to these dielectric phenomena were proposed. The rôle of water molecules trapped in

the structure was discussed.

Rock-forming Minerals and Petrology

30032. **Aoki (Ken-ichiro) & Matsumoto (Hatao):** *On kaersutite from the Iki Island, Nagasaki Prefecture.* Jour. Jap. Asso. Min. Petro. & Econ. Geol., **43**, 248–253 (1959).

Kaersutite is found in trachybasalt, trachyandesite, trachyte and alkali rhyolite of the Iki Island. Kaersutite bearing rocks were studied by chemical method and kaersutites were also chemically analysed. The writers proposed a name oxykaersutite for this mineral, which shows high ratio of Fe_2O_3/FeO and high refractive indices with strong pleochroism.

30033. **Kumagai (Naoiti) & Ito (Hidemumi):** *On the p-T diagrams of the trimorphic minerals of Al_2SiO_5 with a special reference to andalusite and cyanite as a geologic thermometer or a geologic piezometer.* Mem. Coll. Sci. Univ. Kyoto, Ser. B, **26**, 215–223 (1959).

From differences in Gibbs free energies calculated by the second law of thermodynamics, the p-T diagrams are given with reference to sillimanite, andalusite and cyanite, the trimorphic minerals of Al_2SiO_5.

It is suggested that andalusite is stable at high temperature—low pressure, cyanite at high pressure—low temperature, and sillimanite at the intermediate ranges. The temperature of magma from which the andalusite bearing granite is made should be above 1760°K. The pressure of dynamometamorphism producing cyanite should be about 50,000 atm. The impurities in these minerals give some effects on the diagram.

30034. **Seki (Yotaro):** *Petrographic studies on the Circum-Hida crystalline schist* I—*Crystalline schists in the Gamata and Naradani district, Gifu Prefecture.* Sci. Rept. Saitama Univ., Ser. B, **3**, 209–220 (1959).

Low grade metamorphic rocks comprising black and green schists are developed along the outside area of the Hida metamorphic complex in the district. Chlorites from these crystalline schists were analysed with the following results: Chlorite from a black schist; SiO_2 27.40, Al_2O_3 20.19, Fe_2O_3 3.29, FeO 22.01, MnO 1.40, MgO 14.31, CaO 0.00, $H_2O(+)$ 12.03, $H_2O(-)$ 0.08, total 100.81, $\beta=1.635$, $\gamma-\alpha=0.05$, optically positive, $d_{004}=3.537$Å. Chlorite from a green schist of basic volcanic origin; SiO_2 26.56, Al_2O_3 26.76, Fe_2O_3 2.02, FeO 18.24, MnO 0.04, MgO 13.94, CaO 0.34, $H_2O(+)$ 11.96, $H_2O(-)$ 1.02, total 100.88, $\beta=1.628$, $\gamma-\alpha=0.001$, optically negative, $d_{004}=3.534$Å. Chlorite from another green schist; SiO_2 26.75, Al_2O_3 19.65, Fe_2O_3 4.00, FeO 19.43, MnO 1.13, MgO 15.96, CaO 0.00, $H_2O(+)$ 12.42, $H_2O(-)$ 1.09, total 100.43, $\beta=1.628$, $\gamma-\alpha=0.002$, optically negative, $d_{004}=3.539$.

30035. **Tsutsumi (Tokudo):** *The radioactive accessory minerals and their distribution in some granites*

in Japan. Mem. Coll. Sci. Univ. Kyoto, Ser. B, 26, 111-151 (1959).

The distribution of radioactive accessory minerals in fifteen granite bodies were examined by the autoradiographic method. It was revealed, accordingly, that about eighty per cent grains of the minerals fill the intergranular spaces of the principal constituents.

Topographic Mineralogy

30036. **Sakamaki (Yukio):** *Bindheimite from Chichibu Mine.* Kobutsugaku Zasshi, 4, 310-312 (1959).

Bindheimite was found in the Chichibu mine, Saitama Prefecture in Japan. Under the microscope, it is yellowish brown and transparent. X-ray data are in good agreement with those obtained by Mason.

Various Topics

30037. **Tsusue (Akio):** *Paragenesis of minerals of ludwigite series.* Jour. Jap. Asso. Min. Petro. Econ. Geol., 43, 309-317 (1959).

Mode of occurrence of paigeite from the Kamaishi mine, Iwaté Prefecture and the difference in the paragenesis of paigeite and ludwigite are described. Assuming a similarity of temperature, pressure and chemical potentials of H_2O, CO_2, Na_2O, K_2O, B_2O_3 in pore fluids during the formation of paigeite and ludwigite, it has been concluded that the paigeite and associated minerals were formed where the chemical potential of O_2 in pore fluids was low while that of Fe in the system was high, whereas, the ludwigite, vice versa.

Abstractors

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